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(71) Applicant (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US];
1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **ZHU, Reiyao**
[US/US]; 6101 Lilting Branch Way, Moseley, Virginia
23120 (US).

(74) Agent: **GOLIAN, Andrew, G.**; E. I. du Pont de Nemours
and Company, Legal Patent Records Center, 4417 Lan-
caster Pike, Wilmington, Delaware 19805 (US).

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(54) Title: CRYSTALLIZED META-ARAMID BLENDS FOR FLASH FIRE AND ARC PROTECTION HAVING IMPROVED COMFORT

(57) Abstract: A yarn, fabric, and garment suitable for use in arc and flame protection and having improved flash fire protection 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 flame-retardant rayon fiber, (c) 10 to 20 weight percent modacrylic fiber, (d) 0 to 5 weight percent para-aramid fiber, and (e) 0 to 3 weight percent antistatic fiber based on the total weight of components (a), (b), (c), (d), and (e). 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.



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TITLE OF INVENTION

CRYSTALLIZED META-ARAMID BLENDS FOR FLASH FIRE AND ARC PROTECTION HAVING IMPROVED COMFORT

BACKGROUND OF THE INVENTION**1. Field of the Invention**

This invention relates to a blended yarn useful for the production of fabrics that have arc, flame, and flash fire protective properties, but also have improved comfort. This invention also relates to garments produced with such fabrics.

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 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 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 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 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.

Unfortunately, increasing the performance of such protective apparel can make them more uncomfortable to wear and increase the physical stress on already stressed emergency responders. In some industrial situations workers may actually forego protection because of comfort issues. Therefore, any improvement that provides improved comfort to this high performance apparel without sacrificing flame, flash fire, or arc protection is desired.

SUMMARY OF THE INVENTION

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This invention 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 flame-retardant rayon fiber, (c) 10 to 20 weight percent modacrylic fiber, (d) 0 to 5 weight percent para-aramid fiber, and (e) 0 to 3 weight percent antistatic fiber based on the total weight of components (a), (b), (c), (d), and (e). 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).

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In one embodiment, garments made from the yarn provide thermal protection such that a wearer would experience less than a 60 percent predicted body burn when exposed to a flash fire exposure of 4 seconds per ASTM F1930, while maintaining a Category 2 arc rating.

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DETAILED DESCRIPTION OF THE INVENTION

This invention relates to providing a yarn from which comfortable fabrics and garments can be produced that provide both arc protection and 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 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.

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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.

The yarns consist essentially of a blend of meta-aramid fiber, flame-retardant (FR) rayon fiber, modacrylic fiber, and optionally, small portions of para-aramid fiber and antistatic fiber. Typically, yarns consist of 50 to 80 weight percent meta-aramid fiber with a degree of crystallinity of at least 20%, 10 to 30 weight percent FR rayon fiber, and 10 to 20 weight percent modacrylic fiber. The yarns can also contain 0 to 5 weight percent para-aramid fiber and 0 to 3 weight percent antistatic fiber. In some preferred embodiments, the yarns consist of 55 to 75 weight percent meta-aramid fiber with a degree of crystallinity of at least 20%, 15 to 25 weight percent FR rayon fiber, 15 to 20 weight percent modacrylic fiber, 3 to 5 weight percent para-aramid fiber, and 2 to 3 weight percent antistatic fiber. The above percentages are on a basis of the five named components, that is, the total weight of these five named components in the yarn. 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.

It is believed the use of flame-retardant rayon in the fiber blend adds a fiber component to the yarn that has high moisture regain, which imparts more comfort to the wearer of garments made from fabrics containing the yarn. Fabrics made with FR rayon fiber, while having good fire retardancy and flash fire performance, are not known for having the highest arc performance. Surprisingly, it has been found that if the FR rayon fiber is combined with modacrylic fiber in the blend in the claimed percentages, fabrics and garments having both improved moisture regain and comfort can be obtained while retaining fire high arc rating

performance, high fire retardancy, and in some instances improved flash fire performance.

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--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-aramid are those aramids where the amide linkages are in the meta-position relative to each other, and 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 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 the form of conventional shirts, pants, and coveralls. 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 preferred maximum amount of meta-aramid fibers is 75 weight percent or less; however, amounts as high as 80 weight percent can be used.

By flame-retardant rayon fiber, it is meant a rayon fiber having one or more flame retardants and having a fiber tensile strength of at least 2 grams per denier. Cellulosic or rayon fibers containing as the flame retardant a silicon dioxide in the form of polysilicic acid are specifically excluded because such fibers have a low fiber tensile strength. Also, while such fibers are good char formers, in relative terms their vertical flame performance is worse than fibers containing phosphorous compounds or other flame retardants.

Rayon fiber is well known in the art, and is a manufactured fiber generally composed of regenerated cellulose, as well has regenerated cellulose in which substituents have replaced not more than 15% of the hydrogens of the hydroxyl groups. They include yarns made by the viscose process, the cuprammonium process, and the now obsolete nitrocellulose and saponified acetate processes; however in a preferred embodiment the viscose process is used. Generally, rayon is obtained from wood pulp, cotton linters, or other vegetable matter dissolved in a viscose spinning solution. The solution is extruded into an acid-salt coagulating bath and drawn into continuous filaments. Groups of these filaments may be formed into yarns or cut into staple and further processed into spun staple yarns. As used herein, rayon fiber includes what is known as lyocell fiber.

Flame retardants can be incorporated into the rayon fiber by adding flame retardant chemicals into the spin solution and spinning the flame retardant into the rayon fiber, coating the rayon fiber with the flame retardant, contacting the rayon fiber with the flame retardant and allowing the fiber to absorb the flame retardant, or any other process that incorporates a flame retardant into or with a rayon fiber. Generally speaking, rayon fibers that contain one or more flame retardants are given the designation "FR," for flame retardant. In a preferred embodiment, the FR rayon has spun-in flame retardants.

The FR rayon has a high moisture regain, which provides a comfort component to fabrics. It is believed that the yarn should have at least 10 weight percent FR rayon to provide detectable improved comfort in the fabrics. Further, while larger percentages of FR rayon might provide even

more comfort, it is believed that if the amount of FR rayon exceeds about 30 weight percent in the yarn, the fabric could have negative performance issues that would outweigh any comfort improvement. In some preferred embodiments the FR rayon fiber is present in the yarn in an amount of 15
5 to 25 weight percent.

The FR rayon fiber can contain one or more of a variety of commercially available flame retardants; including for example certain phosphorus compounds like Sandolast 9000® available from Sandoz, and the like. While various compounds can be used as flame retardants, in a
10 preferred embodiment, the flame retardant is based on a phosphorus compound. A useful FR rayon fiber is available from Daiwabo Rayon Co., Ltd., of Japan under the name DFG "Flame-resistant viscose rayon". Another useful FR rayon fiber is available from Lenzing AG under the name of Viscose FR (also known as Lenzing FR® available from Lenzing
15 Fibers of Austria).

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 weight percent of a halogen-containing vinyl monomer. The halogen-
20 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, methylacrylamide, vinyl acetate, etc.

25 The preferred modacrylic fibers are copolymers of acrylonitrile combined with vinylidene chloride, the copolymer having in addition an antimony oxide or antimony oxides for improved fire retardancy. Such useful modacrylic fibers include, but are not limited to, fibers 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
30 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.

Within the yarns, modacrylic fiber provides a flame resistant char forming fiber with an LOI typically at least 28 depending on the level of doping with antimony derivatives. 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 20 weight percent.

Meta-aramid fiber provides additional tensile strength to the yarn and fabrics formed from the yarn. Modacrylic and meta-aramid fiber combinations are highly flame resistant but do not 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.

It is critical that the meta-aramid fiber have 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 available from E. I. du Pont de 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 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 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 known can be determined from this linear relationship:

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

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 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:

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

where I(1650 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.

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 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 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 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.

The addition of para-aramid fibers in the yarn can provide fabrics formed from the yarn some additional resistance to shrinkage and break-open after flame exposure. Larger amounts of para-aramid fibers in the yarns can make garments comprising the yarns uncomfortable to the wearer. The yarn has 0 to 5 weight percent para-aramid fibers, and in some embodiments, the yarn has 3 to 5 weight percent para-aramid fibers.

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. Illustrative examples are steel fiber, carbon fiber, or a carbon combined with an existing fiber. The antistatic component is present in an amount of 0 to 3 weight percent of the total yarn. 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.

Staple 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, provided the required degree of crystallinity is present in the final 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. Alternatively, multifilament continuous filament yarns can be used to make the fabric.

To provide protection from the intense thermal stresses caused by electrical arcs it is desirable that 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 at least 1.1 calories per square centimeter per ounce per square yard (0.14 Joules per square centimeter per grams per square meter). In some embodiments the arc resistance normalized for basis weight is preferably at least 1.3 calories per square centimeter per ounce per square yard (0.16 Joules per square centimeter per grams per square meter). In some embodiments the arc resistance normalized for basis weight can be 1.5 calories per square centimeter per ounce per square yard (0.185 Joules per square centimeter per grams per square meter) or greater.

Yarns having the proportions of meta-aramid fiber, FR rayon fiber, and modacrylic fiber, and optionally para-aramid fiber and antistatic fiber as previously described, are 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, FR rayon 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.

The yarns used in the making of fabrics consist essentially of the meta-aramid fiber, FR rayon fiber, modacrylic fiber, para-aramid fiber and antistatic fiber as previously described, in the proportions described, and do not include any other additional thermoplastic or combustible fibers or materials. Other materials and fibers, such as polyamide or polyester fibers, provide combustible material to the yarns, fabrics, and garments, and are believed to affect the flash fire performance of the garments.

Garments made from yarns having the proportions of meta-aramid fiber, FR rayon fiber, modacrylic fiber, para-aramid fiber, and antistatic fiber as previously described provide thermal protection to the wearer that is equivalent to less than a 60 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 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 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 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 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 instrumented mannequin using the test protocol of ASTM F1930. The
5 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
10 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.

It is believed the use of crystalline meta-aramid fiber in the yarns, fabrics, and garments as previously described not only can provide
15 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 crystallinity set forth previously compared to an meta-aramid fiber that has not been treated to increase crystallinity. For
20 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 increases, the amount of material between a potential hazard and the subject to be protected
25 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 yarns as previously described allow the use of lighter weight fabrics in protective apparel, particularly in
30 more comfortable single fabric garments, with improved performance. The basis weight of fabrics that have both the desired arc and flash fire performance is 186.5 g/m² (5.5 oz/yd) or greater, preferably 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). 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
5 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 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
10 standard the fabric shall have a char length of less than 4 inches.

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.

15 In some particularly useful embodiments, spun staple yarns having the proportions of meta-aramid fiber, FR rayon fiber, modacrylic fiber, para-aramid fiber, and antistatic fiber as previously described, can be used to make flame-resistant garments. In some embodiments the garments can have essentially one layer of the protective fabric made from the spun
20 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
25 processing industries or industrial electrical/utility where an extreme thermal event might occur.

TEST METHODS

30 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
35 Performance Value of Materials for Clothing".

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)".

5 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".

10 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
15 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 made with the test fabric.

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

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
25 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 industrial washing machine for 20 minutes with a water temperature of 140 degrees F.

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

EXAMPLES

Comparative Example A

This example illustrates a yarn, fabric, and garment having a majority of meta-aramid fiber having a degree of crystallinity that is at least 20%, combined with a minority of modacrylic fiber, para-aramid fiber, and antistatic fiber. This material has both the desired arc rating of 2 and a instrumented thermal mannequin predicted body burn at 4 seconds exposure of < 60%.

A durable arc and thermal protective fabric is prepared having in the both warp and fill airjet spun yarns of intimate blends of Nomex® type 450 fiber, Kevlar® 29 fiber, modacrylic fiber, and antistatic fiber. Nomex® type 450 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 6.8% antimony (known commercially as Protex®C). The Kevlar® 29 fiber is poly(p-phenylene terephthalamide) (PPD-T) fiber and the antistatic fiber is a carbon-core nylon-sheath fiber known commercially as P140.

A picker blend sliver of 68.6 weight percent of Nomex® type 450 fiber, 10 weight percent of Kevlar® 29 fiber, 25 weight percent of modacrylic fiber and 1.4 weight percent P140 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.

The yarn is then used as in the warp and fill of a fabric that is made on a shuttle loom in a 2x1 twill construction. The greige twill fabric has a basis weight of 203 g/m² (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 basis weight of 220 g/m² (6.5 oz/yd²). A portion of this fabric is then tested for its arc, thermal and mechanical properties, and a portion is converted into single-layer protective coveralls for flash fire testing.

Comparative Example B

Comparative Example A is repeated, except an identical amount of FR rayon fiber is substituted in the intimate blend for modacrylic fiber. The
5 FR rayon fiber is Lenzing FR viscose. A portion of this fabric is then tested for its arc, thermal and mechanical properties, and a portion is converted into single-layer protective coveralls for flash fire testing.

Example 1

10 The method shown in Comparative Examples A & B is repeated to make a yarn, fabric, and garment, except that a fiber blend of 55.8 weight percent of Nomex® type 450 fiber, 3% Kevlar® type 29 fiber, 23 weight percent FR rayon fiber, 17 weight percent of modacrylic fiber, and 1.2 weight percent P140 fiber is prepared. A portion of this fabric is then
15 tested for its arc, thermal and mechanical properties, and a portion is converted into single-layer protective coveralls for flash fire testing.

The Table summarizes the expected performance of the yarns, fabrics, and garments described in the examples. Data for nominal basis weight and arc category is given, while predicted body burn and moisture
20 regain properties are relatively rated with items showing improvement given a (+) versus the standard, which is shown with a (o).

Comparative Example A has a good arc rating but only standard comfort and flash fire performance. Comparative Example B has a poorer arc rating but improved comfort and improved flash fire performance.
25 Example 1 has a good arc rating, improved comfort, and improved flash fire performance. The fabric of Example 1 had a surprisingly superior arc testing performance of 10.7 calories per square centimeter, which was better than the arc testing performance of the fabric of Comparative Example A, which was 10.3 calories per square centimeter. On a weight
30 basis Example 1 had a arc performance of 1.65 calories per square centimeter per ounce per square yard (0.203 Joules per square centimeter per grams per square meter), while Example A had an arc performance of 1.58 calories per square centimeter per ounce per square yard (0.195 Joules per square centimeter per grams per square meter).

TABLE

	Example A	Example B	Example 1
Nominal Basis Weight (opsy)	6.5	6.5	6.5
ARC rating (category)	2	1	2
Instrumented Thermal Mannequin Predicted Body Burn at 4sec.	0	+	+
Moisture Regain (Comfort)	0	+	+

CLAIMS

What is claimed is:

- 5 1. A yarn for use in arc and flame protection consisting essentially of:
- (a) 50 to 80 weight percent meta-aramid fiber having a degree of crystallinity of at least 20%;
- (b) 10 to 30 weight percent flame-retardant rayon fiber;
- 10 (c) 10 to 20 weight percent modacrylic fiber;
- (d) 0 to 5 weight percent para-aramid fiber; and
- (e) 0 to 3 weight percent antistatic fiber;
- said percentages on the basis of components (a), (b), (c), (d) and (e).
- 15 2. The yarn of claim 1 with the meta-aramid fiber has a degree of crystallinity in a range from 20 to 50%.
3. A fabric suitable for use in arc and flame protection comprising a yarn consisting essentially of:
- 20 (a) 50 to 80 weight percent meta-aramid fiber having a degree of crystallinity of at least 20%;
- (b) 10 to 30 weight percent flame-retardant rayon fiber;
- (c) 10 to 20 weight percent modacrylic fiber;
- 25 (d) 0 to 5 weight percent para-aramid fiber; and
- (e) 0 to 3 weight percent antistatic fiber;
- said percentages on the basis of components (a), (b), (c), (d) and (e);
- the fabric having a basis weight in the range of 186.5 to 237 grams per square meter (5.5 to 7 ounces per square yard).
- 30 4. The fabric of claim 3 wherein the meta-aramid fiber has a degree of crystallinity in a range from 20 to 50%.
5. The fabric of claim 3 having a char length according to
- 35 ASTM D-6413-99 of less than 6 inches.

6. The fabric of claim 3 having arc resistance according to ASTM F-1959-99 of at least 1.1 calories per square centimeter per ounce per square yard of fabric.

5

7. The fabric of claim 6 wherein the arc resistance is at least 1.3 calories per square centimeter per ounce per square yard of fabric.

8. A garment suitable for use in arc and flame protection comprising a fabric consisting essentially of:

10

- (a) 50 to 80 weight percent meta-aramid fiber having a degree of crystallinity of at least 20%;
- (b) 10 to 30 weight percent flame-retardant rayon fiber;
- (c) 10 to 20 weight percent modacrylic fiber;
- (d) 0 to 5 weight percent para-aramid fiber; and optionally
- (e) 0 to 3 weight percent antistatic fiber;

15

said percentages on the basis of components (a), (b), (c), (d) and (e); the fabrics having a basis weight in the range of 186.5 to 237 grams per square meter (5.5 to 7 ounces per square yard).

20

9. The fabric of claim 8 wherein the meta-aramid fiber has a degree of crystallinity in a range from 20 to 50%.

10. The garment of claim 8, providing 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.

30

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/031143A. CLASSIFICATION OF SUBJECT MATTER
INV. D02G3/04 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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010/009186 A1 (ZHU REIYAO [US]) 14 January 2010 (2010-01-14) the whole document	1-10
A	----- WO 2007/014291 A2 (DU PONT [US]; ZHU REIYAO [US]; GUCKERT DEBBIE [US]; LOVASIC SUSAN L [U]) 1 February 2007 (2007-02-01) cited in the application claim 1 -----	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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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.

"&" document member of the same patent family

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Pollet, Didier

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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