(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 October 2013 (03.10.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/148653 A1

(51) International Patent Classification:
D06P 3/82 (2006.01) *D06P 1/00* (2006.01)
D06P 3/24 (2006.01) *D06M 13/282* (2006.01)

(21) International Application Number:
PCT/US2013/033841

(22) International Filing Date:
26 March 2013 (26.03.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/616,263 27 March 2012 (27.03.2012) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2013/148653 A1

(54) Title: DYEING AND PRINTING OF FABRICS INCLUDING PARTIALLY AROMATIC POLYAMIDES

(57) **Abstract**: An article exhibiting flame resistant or flame retardant (FR) property including a fabric that has received a pre-treatment applied dye or print or combinations thereof; and a post-treatment applied FR additive. The fabric includes a primary yarn including a fiber having vapor phase action and a partially aromatic polyamide fiber.

DYEING AND PRINTING OF FABRICS INCLUDING PARTIALLY AROMATIC POLYAMIDES

FIELD OF THE INVENTION

[0001] The invention relates to dyeing and finishing fabrics including flame resistant/ flame retardant (FR) fabrics that include partially aromatic polyamide fibers and a fiber exhibiting vapor phase action, such as cellulose fibers that have received FR treatment.

BACKGROUND OF THE TECHNOLOGY

[0002] Flame retardant and flame resistant (FR) fabrics are crucial in both military and non-military environments. Firefighters, race car drivers, and petro-chemical workers are just a few of the non-military groups that benefit from the added protection of flame retardant fabrics. However, today the true benefit of flame retardant fabrics lies with the military. In addition to the unforgiving surroundings that military troops must operate in, the advent of unconventional modern warfare creates an even more hostile environment. Specifically, the use of improvised explosive devices ("IEDs") to immobilize large convoys of soldiers makes individual troop protection critically important.

[0003] In addition to ballistic fabrics and body armor, flame retardant fabrics serve a crucial role in protecting soldiers from IEDs. IEDs are constructed of numerous materials (e.g. high-explosive charges, flammable liquids, shrapnel, etc.), some acting as projectiles and others acting as incendiaries upon detonation. Thus, military fabrics must be of varied construction to handle the multitude of threats from an IED.

[0004] There are basically two types of flame retardant fabrics used in protective clothing: (1) Fabrics made from flame retardant organic fibers (e.g. aramid, flame retardant rayon, polybenzimidazole, modacrylic etc.); and (2) Flame retardant fabrics made from conventional materials (e.g. cotton) that have been post treated to impart flame retardancy. Nomex® and Kevlar® aromatic polyamides are among the most common types of flame retardant synthetic fibers. These are made by solution spinning a meta- or para- aromatic polyamide polymer into fiber. Aromatic polyamides do not melt under extreme heat, are naturally flame retardant, but must be solution spun. Unfortunately, Nomex® and KEVLAR® are not very comfortable and are difficult and expensive to produce.

[0005] Another fiber used in protective clothing is modacrylic which is fiber comprising 30 to 70 parts by mass of acrylonitrile and 70 to 30 parts by mass of a monomer such as a halogen-containing vinylidene monomer and/or a halogen-containing vinyl monomer. Commercial examples include PROTEX® C and PROTEX® M fibers manufactured by Kaneka. At an approximate 1:1 blend ratio, modacrylic fibers are known to impart flame resistance properties to fabrics comprising non-FR treated cellulosic fibers such as cotton and lyocell. Examples can be found in EP1498522 and WO2008027454.

[0006] Cellulose fibers such as acetate, rayon, lyocell, and cotton can be rendered flame resistant by incorporating phosphorus-nitrogen additives at fiber spinning or at fabric finishing. The mechanisms for flame resistance performance of both modacrylic and flame resistant cellulose rely on gases emitted from the fibers which dilute, cool, or chemically neutralize flammable gases (vapor phase action) and which form intumescent char barriers (condensed phase action).

[0007] Post-treatment flame retardants are applied to fabrics and can be broken down into two basic categories: (1) Durable flame retardants; and (2) Non-durable flame retardants. For protective clothing, the treatment must withstand laundering, so only durable treatments are selected. Today, most often, durable flame retardant chemistry relies on phosphorus-based FR agents and chemicals or resins to fix the FR agents to the fibers.

[0008] Co-pending U.S. Provisional Patent Application Nos. 61/530,434 and PCT Patent Application No. PCT/US11/52557, filed on September 21, 2011, disclose flame retardant fabrics which include partially aromatic polyamide fibers. These fabrics can also include cellulosic fibers and provide protection required of FR fabrics and garments.

[0009] U.S. Patent No. 6,132,476 discloses the dyeing of FR fabrics and garments, but acknowledges that when these fabrics include certain inherently flame resistant fiber such as aromatic polyamides in combination with fibers such as FR rayon, the dyeing process reduces the effectiveness of the FR properties. The reason is that the high temperatures required for dyeing aromatic polyamides cause depletion of the FR agents in the FR rayon and make the fabrics more susceptible to further depletion of the FR additive during subsequent laundering. Specific dyeing processes and conditions are required to avoid these concerns.

SUMMARY OF THE INVENTION

[0010] There is an ongoing need for fabrics that provide necessary FR properties that avoid the concerns of reduction of FR properties of the fabric during dyeing and/or subsequent laundering. Ideally, these new processes provide flexibility in the selection of a dyeing and/or printing process while providing and maintaining desired and/or required flame resistant or flame retardant properties.

[0011] One aspect provides an article which has been dyed and/or printed exhibiting flame resistant or flame retardant property including a primary yarn; where the primary yarn includes a flame resistant or flame retardant (FR) fiber having significant vapor phase action such as modacrylic or FR cellulose fibers and a fiber different from said flame resistant or flame retardant fiber including a partially aromatic polyamide fiber; where the partially aromatic polyamide polymer without FR additives is melt spun into fiber. In other words, the partially aromatic polyamide fiber excludes FR additives, which are integral to the fiber composition. The article may be a yarn. However, the article may also be a fabric or a garment including the flame resistant yarn.

[0012] Another aspect provides an article exhibiting flame resistant or flame retardant (FR) property including (a) a fabric including a pre-treatment applied dye or print or combinations thereof; and (b) a post-treatment applied FR additive; wherein the fabric includes a primary yarn comprising a fiber having vapor phase action and a partially aromatic polyamide fiber. The pre-treatment is selected from the group consisting of a dye, a print, or combinations thereof and is present on the garment prior to the addition of the post-treatment which includes an FR additive. In other words there are few limitations on the dyeing process that can be used as depletion of the FR is not an issue because the article receives an FR treatment subsequent to the dyeing. However, where printing is desired, the print may be applied before or after the application of the FR treatment because the printing process does not interfere with the FR treatment in the manner that high temperature dyeing may.

[0013] In a further aspect is an article exhibiting flame resistant or flame retardant property including (a) a fabric including a pre-treatment consisting of dyeing, printing, and combinations thereof; and (b) a post-treatment including a flame resistant or flame resistant or flame retardant treatment; wherein said fabric includes a primary yarn including a cotton fiber and a partially aromatic polyamide fiber.

[0014] A method for preparing an article exhibiting flame resistant or flame retardant property including the following sequential process (a) preparing a fabric including primary yarn comprising a fiber having vapor phase action and a partially aromatic polyamide fiber; (b) providing a pre-treatment selected from the group consisting of dyeing, printing, and combinations thereof; and (c) a post-treatment including a flame resistant or flame resistant (FR) treatment. An optional subsequent process for printing may be introduced following the post-treatment application of FR additive.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The terms “flame resistant,” “flame retardant,” and “FR” have subtle differences in the art. The differences in the usage of the terms relate to describing fabrics which either resist burning, burn at a slower rate and are capable of self-extinguishing under conditions such as a vertical flame test. For the purposes of this invention the terms “flame resistant” and “flame retardant” are used interchangeably and are meant to include any fabric that possesses one or more of the desired properties such as resistance to burning, slow burning, self-extinguishing, etc.

[0016] The term “vapor phase action” for fibers useful in the present invention is meant to include fibers which dilute, cool, or chemically neutralize flammable gases. The mechanisms for flame resistance performance of both modacrylic and flame resistant cellulose rely on gases emitted from the fibers which dilute, cool, or chemically neutralize flammable gases (vapor phase action) and which form intumescent char barriers (condensed phase actions).

[0017] The articles, specifically, yarns, fabrics and garments exhibit flame resistant and/or flame retardant properties. The yarns include at least one fiber which is a partially aromatic polyamide. The yarn including the partially aromatic fiber is referred to in the claims as a “primary yarn.” The term “primary yarn” is not meant to establish any relative weight percent of yarn in comparison to other yarns that may be present in the article, but instead is used to distinguish the yarn from other yarns. The primary yarn must include a partially aromatic fiber which excludes spun-in FR additives combined with a FR fiber such as a FR cellulose fiber, modacrylic fiber, and mixtures thereof.

[0018] Unexpectedly, it is found that MXD6 polyamide fibers are dye-able using several types of dyes for the pre-treatment applied dye. This enables the dyer/printer/finisher to have extra flexibility in choosing the best and most compatible dyeing chemistry for performance and cost. A wider range of dye and pigment selection permits the dyer to more easily meet stringent military requirements for the IR reflectance of camouflage fabrics. Minimizing IR reflectance is critical to prevent wearer from being seen via IR night vision goggles.

[0019] The articles including a pre-treatment such as a dye or a print or both. The dye may be selected from the group consisting of acid dye, cationic dye, disperse dye, vat dye, and combinations thereof. Where a dye is included, the article may be dyed to a union shade. While the post-treatment step includes an FR treatment, a second FR treatment that occurs during the pre-treatment dyeing or printing may also be provided

[0020] Indications from vertical flammability tests are that dyeing can actually help the flame resistance of MXD6 fabrics. In addition, the morphology of MXD6 fibers may allow FR ingredients (such as cyclic phosphinate esters) to be added at fabric dyeing,

[0021] The partially aromatic fibers may be prepared in the presence or absence of non-halogen flame retardant additives. The spun-in non-halogen flame retardant additives can include: condensation products of melamine (including melam, melem, and melon), reaction products of melamine with phosphoric acid (including melamine phosphate, melamine pyrophosphate, and melamine polyphosphate (MPP)), reaction products of condensation products of melamine with phosphoric acid (including melam polyphosphate, melem polyphosphate, melon polyphosphate), melamine cyanurate (MC), zinc diethylphosphinate (DEPZn), aluminum diethylphosphinate (DEPAl), calcium diethylphosphinate, magnesium diethylphosphinate, bisphenol-A bis(diphenyphosphinate) (BPADP), resorcinol bis(2,6-dixylenyl phosphate) (RDX), resorcinol bis(diphenyl phosphate) (RDP), phosphorous oxynitride, zinc borate, zinc oxide, zinc stannate, zinc hydroxystannate, zinc sulfide, zinc phosphate, zinc silicate, zinc hydroxide, zinc carbonate, zinc stearate, magnesium stearate, ammonium octamolybdate, melamine molybdate, melamine octamolybdate, barium metaborate, ferrocene, boron phosphate, boron borate, magnesium hydroxide, magnesium borate, aluminum hydroxide, alumina trihydrate, melamine salts of glycoluril and 3-amino-1,2,4-triazole-5-thiol, urazole salts of potassium, zinc and iron, 1,2-ethanediyl-4-4'-bis-triazolidine-3,5,dione, silicone, oxides of Mg, Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Sn, Sb, Ba, W, and Bi, polyhedral oligomeric silsesquioxanes, silicotungstic acid (SiTA), phosphotungstic acid, melamine salts of tungstic acid, linear, branched or cyclic phosphates or phosphonates, spirobisphosphonates, spirobisphosphates and nanoparticles, such as carbon nanotubes and nanoclays (including, but not limited to, those based on montmorillonite, halloysite, and laponite).

[0022] When present in the partially aromatic polyamide fiber, the flame retardant additive is present in an amount from about 1% to about 25% w/w, including from about 5% to about 20%

w/w, about 5% to about 10%, and about 10%. The mean particle size of the flame retardant additive is less than about 3 microns, including less than about 2 microns, and less than about 1 micron.

[0023] The particle size of the flame retardant additive may be prepared by a milling process which comprises air jet milling of each component, or of co-milling blends of components to reduce the particle size. Other wet or dry milling techniques known in the art (e.g. media milling) may also be used to reduce additive particle size for fiber spinning. If appropriate, milling may involve the injection of liquid milling aids, possibly under pressure, into the mill at any suitable point in the milling process. These liquid aids are added to stabilize the flame retardant system and/or prevent agglomeration. Additional components to aid in particle wetting and/or prevent re-agglomeration may also be added at any suitable point during the milling of flame retardant additive, the blending of the flame retardant additive and polymer, and/or the fiber spinning process.

[0024] The flame retardant may be compounded with the polymeric material in an extruder. An alternative method involves dispersing the flame retardant composition in polymer at a higher concentration than desired in the final polyamide fiber product, and forming a masterbatch. The masterbatch may be ground or pelletized and the resulting particulate dry-blended with additional polyamide resin and this blend used in the fiber spinning process. Yet another alternative method involves adding some or all components of the flame retardant additive to the polymer at a suitable point in the polymerization process.

[0025] In one aspect, the partially aromatic fibers exclude spun-in FR additives. The partially aromatic polyamide may include polymers or copolymers including monomers selected from the group consisting of aromatic diamine monomers, aliphatic diamine monomers, aromatic diacid monomers, aliphatic diacid monomers and combinations thereof. The partially aromatic polyamide can also include or exclusively be MXD6 which includes an aromatic diamine and non-aromatic diacid. Other partially aromatic polyamides can be based upon an aromatic diacid such as terephthalic acid (polyamide 6T) or isophthalic acid (polyamide 6I) or blends thereof (polyamide 6T/6I). The melting, or processing temperatures, of partially aromatic polyamides ranges from about 240°C (for MXD6) to about 355°C (for polyamideimide), including about 260°C, 280°C, 300°C, 320°C, and 340°C. Nylon 6 and nylon 6,6 have melting temperatures of about 220°C and 260°C, respectively. The lower the melting temperature, the easier the polyamide polymer is to process into fiber. Below is a list of common partially aromatic polymers and certain comparative non-aromatics and their associated melting temperatures.

Polymer	Trade Name	Melting Temperature, °C
Nylon 6 (non-aromatic)	Various	220
Nylon 66 (non-aromatic)	Various	260
MXD6	MXD6	240
Nylon 6/6T	Grivory	295
Polyphthalamide (PPA)	Zytel, LNP	300
Nylon 6T	Arlen	310
Nylon 6I/6T	Grivory	325
Polyamideimide	Torlon	355

[0026] The partially aromatic polyamides may also include co-polymers or mixtures of multiple partially aromatic amides. For example, MXD6 can be blended with Nylon 6/6T prior to forming a fiber. Furthermore, partially aromatic polymers may be blended with an aliphatic polyamide or co-polymers or mixtures of multiple aliphatic polyamides. For example, MXD6 can be blended with Nylon 6,6 prior to forming a fiber. The partially aromatic fiber may include up to about 20% by weight of the fiber of one or more aliphatic polyamides.

[0027] The partially aromatic fiber can be a staple fiber or continuous filament yarn. The partially aromatic fiber can also be contained in a nonwoven fabric such as spun bond, melt blown, or a combination thereof. The filament cross section can be any shape, including round, triangle, star, square, oval, bi-lobal, tri-lobal, or flat. Further, the filament can be textured using known texturing methods. As discussed above, the partially aromatic polyamides spun into fibers can also include additional partially aromatic or aliphatic polymers. When spinning such fibers, a mixture of more than one polyamide polymer may be blended prior to spinning into yarn or a multi- filament yarn may be produced containing at least one partially aromatic polyamide polymer and an additional partially aromatic polyamide polymer or aliphatic polymer in a bicomponent form such as a side-by-side or core-sheath configuration.

[0028] The partially aromatic fiber will be combined with an FR fiber having significant vapor phase action such as modacrylic or FR cellulose fibers to form the primary yarn. The yarn may include only the partially aromatic fiber and the FR fiber; alternatively other fibers which are FR or non-FR fibers may be included. The useful amount of partially aromatic fiber varies. Suitable amounts of partially aromatic fiber include about 5% to about 75% by weight of the primary yarn; about 5% to about 60% by weight of the yarn; and about 25% to about 50% by weight of the yarn. The combined yarn may be prepared by any suitable method. For example, the yarn may be a blended staple yarn. The blended staple yarn may be an intimate blend in which the partially aromatic fiber and FR fiber are uniformly blended throughout the yarn. Alternatively, the yarn may be a single or ply twisted yarn, a covered yarn (including single and double covering) or a core-spun yarn, among others.

[0029] The primary yarn must include at least one FR fiber which is and has significant vapor phase action such as modacrylic or FR cellulose fibers, and combinations thereof. The FR fiber may also be FR cellulose where an FR additive is added to the FR cellulose during fiber manufacturing. Alternatively, an FR treatment may be applied to the article including an untreated cellulosic fiber. Examples of suitable cellulosic fibers include cotton, rayon or lyocell. Articles that include FR cellulose are meant to include those in which a constituent element, such as a yarn, is treated prior to incorporation into an article. Articles that include FR cellulose are also meant to include those treated after combining the cellulose into a yarn, as well as those treated after the yarns have been made into fabric or garments. As used herein, cellulose includes, but is not limited to, acetate, cotton, rayon, lyocell, and combinations thereof. In the primary yarn, one or more cellulosic fibers can be combined with each other and/or with modacrylic. The amounts of FR fiber having significant vapor phase action may vary. Suitable amounts of this fiber include about 25% to about 75% by weight of the primary yarn; greater than 25% to about 75% by weight of the yarn; about 40% to about 60% by weight of the yarn; and about 50% to about 75% by weight of the yarn.

[0030] Regardless of whether FR fiber of the primary yarn has received an FR treatment or additive prior to the pre-treatment step, a post-treatment applied FR additive is introduced to article, fabric or garment, after dyeing. Post-treatment flame retardants include: (1) Durable flame retardants; and (2) Non-durable flame retardants. For protective clothing, the treatment must withstand laundering, so durable treatments are more desirable. Suitable examples of FR treatments for the post-treatment applied FR additive include durable flame retardant chemistry relying on phosphorus-based FR agents and chemicals or resins to fix the FR agents to the fibers.

[0031] One suitable process for FR post-treatment is the "PROBAN" process. "PROBAN" is the trade name for a finishing process in which a cotton-rich fabric is dipped in a water-soluble cross linkable phosphorus-containing resin and cured by ammonia gas or liquid. The process was originally patented by Hooker Chemical in the US and Albright & Wilson in the UK. This process uses tetrakis-(hydroxylmethyl) phosphonium salts wherein the salt component could be sulfate (THPS) or chlorate (THPC). Because of concerns about some by-products, THPS with an ammonia gas curing chamber is the system used today. A benefit of the process is that the FR component is in a very stable phosphine oxide structure. The THPC-urea precondensate is water soluble until it is cross linked by the ammonia treatment. At that point it is well-penetrated into the cotton fibers and insoluble. Wash durability is excellent (up to 100 industrial laundering cycles).

[0032] The primary yarn may also include other FR fibers which are well-known in the art. Typically, these will be combined in a minor amount such as from 0 to about 50% based on the weight of the yarn. Other suitable amounts include greater than 0 such as greater than about 5%, greater than about 10% and up to about 30% by weight of the primary yarn. Examples include, but are not limited to, FR polyester, FR nylon, m-aramid, p-aramid, novoloid, melamine, poly(p-phenylene benzobisoxazole (PBO), polybenzimidazole (PBI), polysulphonamide (PSA), partially oxidized polyacrylonitrile (PAN) and combinations thereof.

[0033] The amount of the partially aromatic fiber in the primary yarn will depend on which FR fiber and/or other fibers (FR or non-FR) are also included in the yarn. For example, the partially aromatic polyamide fiber may be present in said primary yarn in an amount of about 5% to about 75% by weight of the primary yarn; alternatively the partially aromatic polyamide fiber may be present in said primary yarn in an amount of about 5% to about 60% by weight of the primary yarn. Other suitable ranges include where the minimum amount of partially aromatic fiber is about 25%; such as where the amount of partially aromatic fiber is about 25% to about 75% by weight of the primary yarn or about 25% to about 60% by weight of the primary yarn. The partially aromatic polyamide may also be present in an amount of about 40% to about 60% or about 50% by weight of the primary yarn. The type of FR fiber that accompanies the partially aromatic fiber will contribute to the necessary weight percent of each component based on the total weight of the primary yarn. When the primary yarn is included in a fabric, the fabric self-extinguishes in a vertical flammability test (ASTM D6416). Specifically, the article of one aspect is a fabric capable of having an after-flame time of less than about 10 seconds in a vertical flammability test.

[0034] Additional fibers which may be included within the primary yarn, in staple or filament form (depending on the fiber), both flame retardant and non-flame retardant, are useful for to form other yarns, fabrics and garments. The additional fibers can include cellulose (whether FR or not) such as cotton, rayon or lyocell, para-aramid, meta-aramid, modacrylic, melamine, poly(p-phenylene benzobisoxazole) (PBO), polybenzimidazole (PBI), polysulphonamide (PSA), oxidized acrylic, partially oxidized acrylic (including partially oxidized polyacrylonitrile), novoloid, wool, flax, hemp, silk, nylon (whether FR or not), polyester (whether FR or not) , anti-static fibers, and combinations thereof. Certain fibers, such as para-aramid, PBI, or PBO, maintain strength after flame exposure and, when used in blended yarns and fabrics, are effective at reducing the fabric char length after flammability testing.

[0035] The article of one aspect may further include at least one additional yarn which is compositionally different from said primary yarn. “Compositionally different” means that the additional yarn differs from the primary yarn in at least one of a variety of aspects such as including different fiber compositions, different amounts of the same fibers, different fiber cross-section, different additives, different colors, etc. The article may further comprise at least two additional yarns which are compositionally different from each other and compositionally different from said primary yarn. Also, the additional yarn may be an FR yarn; or may be a non-FR yarn.

[0036] The fabrics made with the primary yarn can also include additional yarns such as cellulose (whether FR or not) including cotton, rayon or lyocell, para-aramid, meta-aramid, modacrylic, melamine, poly(p-phenylene benzobisoxazole) (PBO), polybenzimidazole (PBI), or polysulphonamide (PSA), oxidized acrylic, partially oxidized acrylic (including partially oxidized polyacrylonitrile), novoloid, wool, flax, hemp, silk, nylon (whether FR or not), polyester (whether FR or not) , anti-static fibers, and combinations thereof.

[0037] Fabrics comprising non-FR celluloses can be treated with additional flame retardant additives and finishes if necessary. An exemplary method for treating cotton is found in the technical bulletin ‘Fabric Flame Retardant Treatment’ (2003) published by Cotton Incorporated, Cary, North Carolina, herein incorporated by reference in its entirety. The fabrics can be woven, knit, and non-woven fabrics. Non-woven fabrics include those made from carded webs, wet-lay, or spun bond/melt blown processes.

[0038] The fibers, yarns, and fabrics can also contain additional components such as: UV stabilizers, anti-microbial agents, bleaching agents, optical brighteners, anti-oxidants, pigments, dyes, soil repellants, stain repellants, nanoparticles, and water repellants. UV stabilizers, anti-microbials agents, optical brighteners, anti-oxidants, nanoparticles, and pigments can be added to the flame retardant polymer prior to melt-spinning or added as a post-treatment after fiber formation. Dyes, soil repellants, stain repellants, nanoparticles, and water repellants can be added as a post-treatment after fiber and/or fabric formation. Fabrics made with the disclosed flame retardant fiber may also have a coating or laminated film applied for abrasion resistance or for control of liquid/vapor permeation.

[0039] **Definitions**:

[0040] After flame means: "Persistent flaming of a material after ignition source has been removed." [Source: ATSM D6413-11 *Standard test Method for Flame Resistance of Textiles (Vertical Method)*]

[0041] Char length means: "The distance from the fabric edge, which is directly exposed to flame to the furthest of visible fabric damage, after a specified tearing force has been applied." [Source: ATSM D6413-11 *Standard test Method for Flame Resistance of Textiles (Vertical Method)*]

[0042] Drip means: "A flow of liquid that lacks sufficient quantity or pressure to form a continuous stream." [Source: National Fire Protection Association (NFPA) Standard 2112, 2007 Edition, *Standard on Flame-Resistant Garments for Protection of Industrial Personnel Against Flash Fire*].

[0043] Melt means: 'The response to heat by a material resulting in evidence of flowing or dripping.' [Source: National Fire Protection Association (NFPA) Standard 2112, 2007 Edition, *Standard on Flame-Resistant Garments for Protection of Industrial Personnel Against Flash Fire*].

[0044] Self-Extinguishing means: Material will have no persistent flaming after the ignition source is removed OR flaming shall stop before the specimen is totally consumed.

When tested by ATSM D6413-11 *Standard test Method for Flame Resistance of Textiles (Vertical Method).*

[0045] The features and advantages of the present invention are more fully shown by the following examples which are provided for purposes of illustration, and are not to be construed as limiting the invention in any way.

EXAMPLES

Test Methods:

[0046] Flame retardancy was determined in accordance with ASTM D-6413-11 *Standard Test Method for Flame Resistance of Textiles (Vertical Test).*

Colorfastness to Laundering: American Association of Textile Chemist and Colorists (AATCC) Test Method 61 wherein color transfer to a multi-fiber test strip indicates dye loss from test fabric and staining a multi-fiber test strip comprised on the fibers listed in the tables of Examples. Color loss or adsorption is rated on a Gray Scale (1-5) where 5 is negligible change and 1 is a large change.

Color Measurement: After dyeing, color is read using a Macbeth Color Eye 7000A spectrophotometer which measures visible light spectral reflectance of the sample for brightness, whiteness, and yellowness,

Interpretation of readings is as follows:

- Higher L value indicates lighter shades
- Higher the K/S value indicates darker shades
- a- value: Represents redness, Higher a –value is redder. Lower is more green.
- b- value : Represents yellowness. Higher b –value is yellower, Lower is bluer.

Vertical Flammability: ASTM D6413 'Standard Test Method for Flame Resistance of Textiles (Vertical Test)

[For all examples: Several classes of dyes are used to compare the dyeing characteristics of MXD6 and nylon 66 fibers. Fiber samples were pre-scoured using 1 g/l soda ash and 1 g/l Domoscour LFE-810 at 160°F for 15 minutes.]

Example Set 1: Fibers were dyed individually using milling acid dye with and without a leveling agent. Fibers were dyed for 60 minutes at 212 °F.

Color eye readings for comparative dyeings

	L	**a**	**b**	**K/S**	**DE**	**% Apparent Color strength**
MBB dye (without leveling agent)						
N-66	36.72	25.01	38.52	9.62	0	100
MXD6	35.04	23.10	-39.5	11.02	2.72	115.06
MBB dye (with leveling agent)						
N-66	47.13	19.73	37.33	4.45	0	100
MXD6	51.34	12.76	29.24	2.95	11.47	73.13

Conclusion: ***MXD6 fibers dye darker than N66 when using a*** **milling acid** ***dye without leveling agent.***

Example Set 2: Competitive dyeing. Fibers were dyed in the same bath using disperse Blue 3 dye at pH= 9.0 and acid blue 45(ABB) dye at pH=5.8 and acid blue 122 milling acid (MBB) dye at pH=5.0 with and without anionic leveling agent at pH=5.7. Fibers were dyed for 60 minutes at 212 °F.

Color eye readings for various dye classes

	L	**a**	**b**	**K/S**	**DE**	**% Apparent Color strength**
Disperse dye						
N-66	43.54	14.11	-2.86	4.68		100
MXD6	43.21	12.67	-6.15	4.39	2.86	101.75
ABB acid dye						
N-66	35.64	-2.49	37.94	18.31		100
MXD6	57.61	-2.99	-2.95	2.97	28.6	17.7
MBB acid dye (without leveling agent)						
N-66	31.53	30.02	-41.7	14.86		100
MXD6	38.64	20.03	-6.96	8.16	13.15	56.11
MBB dye (with leveling agent)						
N-66	43.93	22.23	-9.32	5.74		100
MXD6	44.2	17.43	-4.84	5.32	6.57	97.02

Conclusions:

1. ***Using anthraquinon milling blue B (ABB Type amine end group sensitive dyestuff), MXD6 dyes 80 % lighter vs. control N-66.***
2. ***Using milling blue BL (MBB type structure sensitive dyestuff) without leveling agent, dyes 20% lighter than control. Dyes similar to N66 with leveling agent.***

Example Set 3: Dyeing with cationic dyes. Fibers were dyed in separate baths using one of two dye formulas:

Blue: 1% Astrazon Blue F2RL 200%, 2 g/l Laurotex A-25, pH= 4.5, 0.5% Domoscour LFE-810 at 212°F for 60 minutes

Red: 1% Maxilon Red GRL 200%, 2 g/l Laurotex A-25, pH= 4.5, 0.5% Domoscour LFE-810 at 212°F for 60 minutes

Color eye readings cationic dye shades

	L	**a**	**b**	**K/S**	**DE**	**% Apparent Color strength**
Blue Dye:						
N-66	*43.57*	-0.41	-35.23	6.2	0	100
MXD6	*27.49*	10.33	-43.24	23.7	20.93	380
Red Dye:						
N-66	*72.23*	9.88	2.46	0.48	0	100
MXD6	*63.04*	33.72	1.18	1.65	25.57	219

Staining and washfastness of cationic dyes

	Acetate	**Cotton**	**Nylon**	**Polyester**	**Acrylic**	**Wool**	**Shade Change**
Blue:							
N-66	*5*	*5*	4	5	5	4	4--5
MXD6	*5*	*4*	4	5	5	4	4--5
Red:							
N-66	5	5	5	5	5	5	4--5
MXD6	4	4	4	5	5	4	4--5

***Conclusion**: MXD6 dyes darker with cationic dyes than nylon 66. However, dye is not as washfast as acid dyes.*

Example Set 4: Dyeing with acid dyes. Fibers were dyed in separate baths using one of two acid dye formulas:

Navy (pre-metallized): 3% Lanaset Navy 2R + 0.2% Lanaset Orange RN, pH= 5.0, 0.25% Albegal B, 2 g/; Laurotex A-25, 212F for 60 minutes.

Red: 2% Erionyl Red 3G + 0.5% Polar Red 3BN 140% , pH= 5.0, 0.25% Albegal B, 2 g/; Laurotex A-25, 212F for 60 minutes.

Dark Green: 2% Nylon Turq. GLM + 0.5% Supernol Navy R + 1% Telon Yellow A-3gL. pH= 5.0, 0.25% Albegal B, 2 g/; Laurotex A-25, 212F for 60 minutes.

After dyeing, 3% Nylofixan MF2N at 170F, pH= 4.5 for 20 minutes was used to affixed the dyes.

Color eye readings for acid dyes

	L	a	b	K/S	DE	% Apparent Color strength
Navy:						
N-66	21.32	1.62	-12.33	18.02	0	100
MXD6	23.37	-0.98	-14.25	16.55	3.84	89.8
Green:						
N-66	23.14	-15.91	-1.7	27.58	0	100
MXD6	31.18	-22.22	-2.33	29.31	11.59	71.82
Red:						
N-66	34.92	52.55	26.09	24.91	0	100
MXD6	36.72	55.28	20.21	23.58	6.72	81.64

Staining and Washfastness of acid dyes

	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool	Shade Change
Navy							
N-66	5	5	5	5	5	5	4--5
MXD6	5	5	5	5	5	5	4--5
Green:							
N-66	5	5	5	5	5	5	4--5
MXD6	5	5	5	5	5	5	4--5
Red:							
N-66	5	5	5	5	5	5	4--5
MXD6	5	5	5	5	5	5	4--5

***Conclusion*: Overall acid dye dye-ability of MXD6 nylon is good, although weaker than nylon 66.**

Example Set 5: Dyeing blends of MXD6 and cellulose fibers. Fabric comprising both fibers were dyed using two step processes of a reactive dye for the cellulose fiber and an acid dye for the MXD6 fiber.

Pre-scour/bleach:

1 g/l Domoscour LFE-810 + 1.5 g/l Soda ash + 2 g/l Albone 35 + 0.25 g/l Versene 30A at 200°F for 20 minutes. Rinse

Dyeing cellulose with reactive dyes:

Set bath at 80F. with 2g/l laurotex A-25

Add dyes.

0.56% Novacron Olive C

0.041% Novacron Brown NC

0.08% Novacron Navy FN-BN

Run 5 min. Add 50 g/l salt run 5 min. Raise to 140F, 3 F/min.
Add 15 g/l Soda ash.
Run 45 minutes

Drain – rinse- Soap off at 200°F using 1 g/l Domoscour LFE 810 for 15 min.
Drop- rinse-

Dyeing MXD6 with acid dyes:.
Set bat wit 2 g/l Laurotex A-25 + 0.5% ALbegal B.
3 g/l MSP , ph= 5.5
Run 5 minutes. Add Acid dyes.
0.22% Erionyl Yellow A-3G
0.032% Erionyl Red A-3g
0.16% Erionyl Navy A-R

Run 5 min. Raise to 212°F, 3F/minutes. Run 45 minutes.
Cool—drain- rinse.
Apply 2% Cibafix DGF at 170°F, pH= 4.5 for 20 minutes.

***Conclusion:* The above process yields a good union dyeing of 50/50 MXD6/cellulose fabric.**

[0047] While there have been described what are presently believed to be the preferred embodiments of the invention, those skilled in the art will realize that changes and modifications may be made thereto without departing from the spirit of the invention, and it is intended to include all such changes and modifications as fall within the true scope of the invention.

What is claimed is:

1. An article exhibiting flame resistant or flame retardant (FR) property comprising:

(a) a fabric including a pre-treatment applied dye or print or combinations thereof; and

(b) a post-treatment applied FR additive;

wherein said fabric includes a primary yarn comprising a fiber having vapor phase action and a partially aromatic polyamide fiber.

2. The article of claim 1, wherein said pre-treatment includes a dye selected from the group consisting of acid dye, cationic dye, disperse dye, vat dye, reactive dye and combinations thereof.

3. The article of claim 1, wherein said fabric is dyed to a union shade.

4. The article of claim 1, wherein said pre-treatment further comprises a second FR treatment.

5. The article of claim 1, wherein said partially aromatic polyamide is spun into fiber without FR additives.

6. The article of claim 1, wherein the partially aromatic polyamide comprises polymers or copolymers comprising monomers selected from the group consisting of aromatic diamine monomers, aliphatic diamine monomers, aromatic diacid monomers, aliphatic diacid monomers and combinations thereof.

7. The article of claim 6, wherein the partially aromatic polyamide further comprises aromatic diamine monomers and aliphatic diacid monomers.

8. The article of claim 1, wherein the partially aromatic polyamide is MXD6.

9. The article of claim 1, wherein said partially aromatic polyamide fiber comprises a form selected from the group consisting of staple, continuous filament, and combinations thereof.

10. The article of claim 1, wherein said primary yarn includes a twisted yarn, a ply-twisted yarn, a textured yarn, a blended staple yarn, and combinations thereof.

11. The article of claim 1, wherein said partially aromatic polyamide fiber is present in said primary yarn in an amount of about 5% to about 75% by weight of the primary yarn.

12. The article of claim 1, wherein said fiber having vapor phase action is selected from modacrylic fiber, cellulose fiber, and combinations thereof.

13. The article of claim 1, wherein said primary yarn further includes an additional fiber selected from the group consisting of FR polyester, FR nylon, FR rayon, m-aramid, p-aramid, modacrylic, novoloid, melamine, poly(p-phenylene benzobisoxazole (PBO), polybenzimidazole (PBI), polysulphonamide (PSA), oxidized acrylic, partially oxidized acrylic, and combinations thereof.

14. The article of claim 1, wherein said article is a fabric.

15. The article of claim 1, wherein said article is a garment.

16. The article of claim 1, further comprising at least one additional yarn which is compositionally different from said primary yarn.

17. An article exhibiting flame resistant or flame retardant property comprising:

(a) a fabric including a pre-treatment consisting of dyeing, printing, and combinations thereof; and

(b) a post-treatment including a flame resistant treatment or flame retardant treatment;

wherein said fabric includes a primary yarn comprising a cotton fiber and a partially aromatic polyamide fiber.

18. A method for preparing an article exhibiting flame resistant or flame retardant property comprising the following sequential process:

(a) preparing a fabric including primary yarn comprising a fiber having vapor phase action and a partially aromatic polyamide fiber;

(b) providing a pre-treatment selected from the group consisting of dyeing, printing, and combinations thereof; and

(c) a post-treatment including a flame resistant or flame retardant (FR) treatment.

19. The method of claim 18 further comprising a second printing step following the post-treatment including a flame resistant or flame retardant treatment.

20. The method of claim 18, wherein said fiber having vapor phase action is a cellulosic fiber.

21. The method of claim 20, wherein said cellulosic fiber comprises cotton.

22. The method of claim 18, wherein the pre-treatment further comprising a second FR treatment.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/033841

A. CLASSIFICATION OF SUBJECT MATTER

D06P 3/82(2006.01)i, D06P 3/24(2006.01)i, D06P 1/00(2006.01)i, D06M 13/282(2006.01)i

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)
D06P 3/82; D06M 23/10; B32B 27/04; D06B 1/00; B29C 47/00; D03D 15/00; D06B 1/02; D06M 14/32; D03D 15/12; D06M 11/50; D06P 3/24; D06P 1/00; D06M 13/282

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords : flame resistant, flame retardant, dye, print, vapor phase action, aromatic polyamide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	KR 10-0955341 B1 (S&B CO., LTD.) 29 April 2010 See claim 1.	1-3,6-18,20,21 4,5,19,22
Y	US 2011-0308022 A1 (LI SHULONG et al.) 22 December 2011 See claims 1, 3, 4, 7.	1-3,6-18,20,21
Y	US 2011-0028060 A1 (WAKEMAN MARTYN DOUGLAS et al.) 03 February 2011 See paragraphs [0024], [0025]; claims 1, 6, 10.	6-8,13,16
A	EP 0533931 A1 (TEIJIN LIMITED) 31 March 1993 See claim 1.	1-22
A	KR 10-2009-0008961 A (KOLONGLOTECH. INC.) 22 January 2009 See abstract; claim 1.	1-22

☐ 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 application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"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
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"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

Date of the actual completion of the international search 25 June 2013 (25.06.2013)	Date of mailing of the international search report **01 July 2013 (01.07.2013)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer YANG, In Su Telephone No. 82-42-481-8131

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