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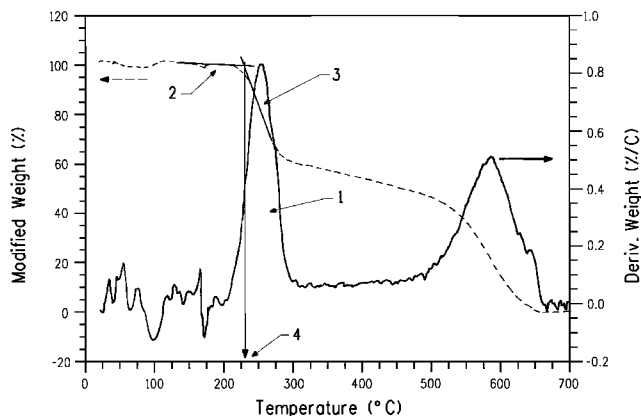


FIG. 1

(57) Abstract: This invention relates to a protective garment and processes for making such a garment, the garment having use in an electrical arc potential environment, the garment having an arc resistant multilayer fabric laminate comprising a first layer of a woven flame-resistant fabric forming an outer surface of the garment and comprising a first fire-resistant fiber made from a synthetic polymer comprising a halogen, and a second layer of a woven flame-resistant fabric comprising a second fire-resistant fiber made from a synthetic polymer, wherein the first fire-resistant fiber has a thermal decomposition temperature that is at least 70 degrees C less than the second fire-resistant fiber; and wherein the fabrics in the first and second layers are different and the first layer is positioned in the garment to be closer the electrical arc potential environment than the second layer.

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TITLE OF INVENTION

5 ARC RESISTANT GARMENT CONTAINING A MULTILAYER FABRIC
 LAMINATE AND PROCESSES FOR MAKING SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention. This invention relates to a multilayer fabric
10 laminate having improved arc performance and protective garments
 containing the multilayer fabric laminate.
2. Description of Related Art. United States Patent Nos. 7,065,950
 and 7,348,059 to Zhu et al. disclose modacrylic/aramid fiber blends for use
15 in arc and flame protective fabrics and garments. Arc resistant garments
 are used in potentially life-threatening situations; as such, any garment
 construction that can provide improved arc protection can potentially
 reduce injury and save lives.

SUMMARY OF THE INVENTION

20 This invention relates to a protective garment having use in an
 electrical arc potential environment, the garment having an arc resistant
 multilayer fabric laminate comprising a first layer of a woven flame-
 resistant fabric forming an outer surface of the garment and comprising a
25 first fire-resistant fiber made from a synthetic polymer comprising a
 halogen, and a second layer of a woven flame-resistant fabric comprising
 a second fire-resistant fiber made from a synthetic polymer, wherein the
 first fire-resistant fiber has a thermal decomposition temperature that is at
 least 70 degrees C less than the second fire-resistant fiber; and wherein
30 the fabrics in the first and second layers are different and the first layer is
 positioned in the garment to be closer the electrical arc potential
 environment than the second layer.

 This invention also relates to a process for making a protective
 garment having use in a electrical arc potential environment, comprising:

- 5
- 10
- 15
- 20
- i) providing a first woven flame-resistant fabric comprising a first fire-resistant fiber made from a synthetic polymer comprising a halogen;
 - ii) providing a second woven flame-resistant fabric comprising a second fire-resistant fiber made from a synthetic polymer, wherein the first fire-resistant fiber has a thermal decomposition temperature that is at least 70 degrees C less than the second fire-resistant fiber; the first and second woven flame-resistant fabrics being different;
 - iii) combining the first and second woven flame-resistant fabrics to form a arc resistant multilayer fabric laminate, the first and second woven flame-resistant fabrics being distinct fabric layers without any shared weft or warp fabric yarns; and
 - iv) forming an arc resistant garment from the arc resistant multilayer fabric laminate wherein the first woven flame-resistant fabric forms an outer surface of the garment and is positioned in the garment closer to the electrical arc potential environment than the second layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 and 2 are thermgravimetric analysis scans in air illustrating how the thermal decomposition temperature of a fiber can be determined.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to protective garments that have use in an electrical arc potential environment. By electrical arc potential environment, it is meant any situation where a worker could be exposed to an electrical arc that could cause injury or death.

This invention relates to a protective garment having an arc resistant multilayer fabric laminate comprising at least two flame-resistant

fabric layers that have different compositions. The first flame-resistant fabric layer forms an outer surface of the garment and comprises a first fire-resistant fiber containing a synthetic polymer comprising a halogen. The second flame-resistant fabric layer comprises a second fire-resistant fiber containing a synthetic polymer. In addition, the first and second fire-resistant fibers have different compositions, and the first fire-resistant fiber has a thermal decomposition temperature that is at least 70 degrees C less than the thermal decomposition temperature of the second fire-resistant fiber.

10 The different fabric compositions provide the multilayer fabric laminate with directionality, and the multilayer fabric laminate is positioned in the garment such that the first flame-resistant fabric layer is closer the electrical arc potential environment than the second flame-resistant fabric layer.

15 Protective garments of this type include protective coats, jackets, jumpsuits, coveralls, hoods, etc. used by industrial personnel such as electricians and process control specialists and others that may work in an electrical arc potential environment. In a preferred embodiment, the protective garment is a coat or jacket, including a three-quarter length coat commonly used over the clothes and other protective gear when work on an electrical panel or substation is required.

In a preferred embodiment, the protective garments have at least a Category 2 arc rating or higher as measured by either of 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 or NFPA 70E.

Electrical arcs typically involve thousands of volts and thousands of amperes of electrical current, exposing the garment to intense incident energy. To offer protection to a wearer, a garment must resist the transfer of this incident energy through to the wearer. It has been believed that this occurs best when the outer shell fabric absorbs a portion of the incident energy while resisting what is called "break-open". During "break-open", a hole forms in the fabric. Therefore, garments for arc protection have been designed to avoid or minimize break-open of any of the fabric layers in the garment.

It has now been found that improved arc performance can be achieved by the use of a multilayer fabric laminate having at least two flame-resistant fabric layers, wherein the fabric layer closer the electrical arc actually acts as a sacrificial material and breaks open upon exposure to the arc. It is believed that the decomposition of the outer fabric provides an energy sink that reduces the transfer of energy through the multilayer fabric laminate.

The multilayer fabric laminate includes at least one layer of the first flame-resistant fabric and at least one layer of the second flame-resistant fabric. In some embodiments, the first flame resistant fabric layer has a basis weight of about 5 to 9 ounces per square yard and the second flame-resistant fabric layer has a basis weight of about 4 to 8 ounces per square yard. In some embodiments, the first flame resistant fabric layer has a basis weight of about 6.5 to 9 ounces per square yard. In some embodiments, the second flame resistant fabric layer has a basis weight of about 4.5 to 7.5 ounces per square yard. In some embodiments, the multilayer fabric laminate can include two adjacent layers of the first flame-resistant fabric and one layer of the second flame-resistant fabric. In some embodiments, the multilayer fabric laminate can include a layer of the first flame-resistant fabric and two adjacent layers of the second flame-resistant fabric. In some other embodiments, the multilayer fabric laminate can include two adjacent layers of the first flame-resistant fabric and two adjacent layers of the second flame-resistant fabric.

By flame-resistant fabric, it is meant that when tested, a layer of the fabric has a vertical char length of 6 inches or more. 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 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.

By fire-resistant fiber, it is meant the fiber or a fabric made solely from that fiber will not support flame, meaning they have a Limiting Oxygen Index (LOI) above the concentration of oxygen in air (that is, greater than 21 and preferably greater than 25) as measured by ASTM G-125-00.

The term fabric refers to a single layer structure that has been assembled by conventional weaving of warp yarns with weft yarns on a loom. One preferred embodiment is a twill weave; however, plain or satin weaves made be used. By yarn is meant an assemblage of fibers spun or twisted together to form a continuous strand that can be used in weaving or knitting, or otherwise made into a textile material or fabric. The yarns can be staple fiber yarns. Staple fiber 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. Alternatively, multifilament continuous filament yarns can be used to make the fabric, or combinations of multifilament and staple fiber yarns can be used.

A first fire-resistant fiber is present in the woven fabric of the first flame resistant fabric layer in an amount of at least 20 percent by weight, and is normally present in the yarns of that fabric. The first fire-resistant fiber contains, and is preferably solely made of, a synthetic polymer comprising a halogen. One useful halogen is chlorine, but other halogens can also be used.

In some embodiments, the first flame resistant fabric contains a blend of yarns, or the yarns contain a blend of fibers, comprising modacrylic fiber, meta-aramid fiber, and para-aramid fiber; and optionally small portions of antistatic fiber. One embodiment of this yarn blend or
5 fiber blend comprises 20 to 70 weight percent modacrylic fiber, 11 to 64 weight percent meta-aramid fiber, 5 to 15 weight percent para-aramid fiber, and optionally 0.5 to 4 weight percent antistatic fiber. If desired, FR rayon, cotton, or wool may be substituted for portions of the modacrylic fiber as long as at least 20 percent of a halogen-containing fiber remains
10 in the first flame resistant fabric. Generally this means these substituted fibers can be present in an amount of up to about 50% of the blend if desired.

In one preferred embodiment, the first flame resistant fabric contains a blend of yarns, or the yarns contain an intimate blend of fibers,
15 comprising 40 to 70 weight percent modacrylic fiber, 15 to 55 weight percent meta-aramid fiber, and 5 to 15 weight percent para-aramid fiber; and optionally contains 0.5 to 3 weight percent antistatic fiber. In some embodiments the blend of yarns or intimate blend of fibers comprises 55 to 70 weight percent modacrylic fiber; 20 to 40 weight percent meta-
20 aramid fiber, the meta-aramid being poly(metaphenylene isophthalamide; 5 to 10 weight percent para-aramid fiber, the para-aramid being poly(paraphenylene terephthalamide); and 2 to 3 weight percent carbon core/polyamide sheath antistatic fiber. In some embodiments, the first flame resistant fabric contain a blend of yarns, or the yarns contain a blend
25 of fibers, consisting essentially of modacrylic fiber, meta-aramid fiber, and para-aramid fiber; and optionally small portions of antistatic fiber in amounts as previously mentioned. All of the percentages stated herein are on a basis of the explicitly named components; that is, the total weight of the named components in the blend of yarns or fibers.

30 A second fire-resistant fiber is present in the woven fabric of the second flame resistant fabric layer and is normally present in the yarns of that fabric. Useful fire-resistant fibers include aramid fiber, polybibenzimidazole fiber, or polybenzazole fiber, or a blend of any of these fibers. In one preferred embodiment, the second flame resistant

5 fabric layer contains at least 70 weight percent of these fibers, and a preferred fiber is meta-aramid fiber. In some preferred embodiments, the yarn has at least 75 weight percent meta-aramid fibers. In some embodiments, the preferred maximum amount of meta-aramid fibers is 93 weight percent or less; however, amounts as high as 100 weight percent can be used.

10 In some embodiments, the second flame resistant fabric contains a blend of yarns, or the yarns contain a blend of fibers, comprising meta-aramid fiber and para-aramid fiber; and optionally, small portions of antistatic fiber. One embodiment of this yarn blend or fiber blend, comprises 70 to 93 weight percent meta-aramid fiber and 7 to 30 weight percent para-aramid fiber. The yarn blend or fiber blend can also contain 0.5 to 3 weight percent antistatic fiber. In some preferred embodiments the yarn blend or fiber blend comprises 85 to 93 weight percent meta-aramid 15 fiber, the meta-aramid being poly(metaphenylene isophthalamide); and 7 to 15 weight percent para-aramid fiber, the para-aramid being poly(paraphenylene terephthalamide); and optionally 2 to 3 weight percent carbon core/polyamide sheath antistatic fiber. The addition of small amounts of rigid rod or para-aramid fibers in the yarns can provide some 20 additional resistance to flame shrinkage for fabrics having a high content of meta-aramid fiber or other fabric having unacceptable flame shrinkage.

25 In one preferred embodiment, the second flame resistant fabric contains a blend of yarns, or the yarns contain an intimate blend of fibers comprising para-aramid fiber and meta-aramid fiber, and optionally small portions of antistatic fiber. In some embodiments, the second flame resistant fabric contains a blend of yarns, or the yarns contain an intimate blend of fibers consisting essentially of para-aramid fiber and meta-aramid fiber, and optionally small portions of antistatic fiber in amounts as 30 previously mentioned. All of the percentages stated herein are on a basis of the explicitly named components; that is, the total weight of the named components in the blend of yarns or fibers.

The antistatic component is an optional component in the garment and can be used in those situations where static electrical discharges can be hazardous for workers, such as when working with sensitive electrical

equipment or near flammable vapors. In one embodiment, the antistatic component is present as a fiber in at least some of the yarns in the garment fabric. Illustrative examples are steel fiber, carbon fiber, or a carbon combined with an existing fiber and can be present in a garment fabric in an amount of 0.5 to 5 weight percent. In some embodiments the antistatic component is present in a garment fabric in an amount of only 2 to 3 weight percent. U.S. Patent 4,612,150 (to De Howitt) and U.S. Patent 3,803453 (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.

In some embodiments, the yarns having the proportions of the first and second fire-resistant fibers and optionally other fibers and/or antistatic fiber, are exclusively present in the fabric. In the case of a woven fabric these yarns are preferably used in both the warp and fill of the fabric. If desired, the relative amounts of of the first and second fire-resistant fibers as previously described and antistatic fiber can vary in the respective warp and fill yarns as long as the compositions of both yarns falls within the previously described ranges.

In one embodiment, both the multilayer fabric laminate, the yarns used in the making of the first and second flame-resistant fabrics, and the fabrics themselves, consist essentially of the fibers as previously described, in the proportions described, and do not include any other additional thermoplastic or combustible fibers or materials, except for small portions of antistatic fibers as previously mentioned. 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 protective performance of the garments.

In environments where additional thermal protection is desired, 1 to 4 layers of a thin flame-resistant insulating fabric can be sandwiched between the first and second flame-resistant fabric and become part of the multilayer fabric laminate as herein defined. Such nonwoven insulating

fabrics can include lightweight (0.5 to 3.0 oz/yd²) needlepunched, hydroentangled, or otherwise consolidated nonwoven fabrics formed from carded, air-laid, or wet-laid cut fiber webs. Preferably, such fabrics have a basis weight of 1 to 2 oz/yd². Especially preferred are fabrics that include
5 fire-resistant fibers. A suitable flame-resistant fabric is Nomex® E89, a spunlaced nonwoven material produced from a blend of meta-aramid and para-aramid staple fibers and available from E. I. du Pont de Nemours & Company of Wilmington, Delaware. E89 fabric has a nominal thickness of 19 mil (0.48 mm) and a basis weight of 1.5 oz/yd² (50.5 g/m²). In one
10 preferred embodiment all of the layers of fabric in the multilayer fabric laminate are sewn together only at the edges and/or seams in the garment, allowing maximum flexibility of the layers of fabric within the multilayer fabric laminate.

In some embodiments, the multilayer fabric laminate has a total
15 basis weight of 11 to 25 ounces per square yard. In some preferred embodiments the total basis weight of the multilayer fabric laminate is 11 to 20 ounces per square yard.

In some preferred embodiments the multilayer fabric laminate has an arc resistance, normalized for basis weight, of at least 2.0 calories per square centimeter per ounce per square yard (0.247 Joules per square centimeter per grams per square meter). In some embodiments the arc
20 resistance normalized for basis weight is preferably at least 2.2 calories per square centimeter per ounce per square yard (0.272 Joules per square centimeter per grams per square meter).

25 One fiber useful as the first fire-resistant fiber is modacrylic fiber. 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-containing
30 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.

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
5 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
10 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 fire resistant, char- forming fiber with an LOI typically at least 28 depending on the level of doping with antimony derivatives.

In addition, other fibers can be present in the first fire resistant fabric layer and these include aramid fibers, flame retardant rayon fibers,
15 cotton fibers, wool fibers, and mixtures of these fibers. These are also normally present in the yarns of the fabric, either in the form of a mixture with, for example, modacrylic fibers, or as separate yarns having only one type of fiber, or separate yarns having a mixture of various fibers.

As used herein, "aramid" is meant a polyamide wherein at least
20 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
25 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.
30 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 meta-aramid includes poly(metaphenylene isophthalamide)

and the para-aramid includes poly(paraphenylene terephthalamide). Within the yarns, meta-aramid fiber provides a fire resistant fiber with an LOI typically at least about 25, with para-aramid fiber having a LOI of at least about 27.

5 In some embodiments, the meta-aramid fiber has a minimum degree of crystallinity of 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
10 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 can be determined by one of two methods. The first method is employed with a
15 non-voided fiber while the second is employed 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
20 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
25 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:

30

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

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 $I(1650 \text{ cm}^{-1})$ 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.

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
5 aramid fibers. Useful dye carriers include aryl ether, benzyl alcohol, or acetophenone.

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
10 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 as 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
20 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
25 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
30 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 10 embodiments the FR rayon fiber is present in the yarn in an amount of 15 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 15 the like. While various compounds can be used as flame retardants, in a 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 20 name of Viscose FR (also known as Lenzing FR® available from Lenzing Fibers of Austria).

Cotton fiber is a well-known natural fiber composed of almost pure natural cellulose. As taken from plants, it has a fiber length of from about 0.375 to 2 inches. Wool fiber is a well-known natural fiber that is normally 25 the fleece of sheep, lambs, or Angora or Cashmire goats. The term can also be used for the hair from the camel, alpaca, llama, and/or vicuna.

By polybibenzimidazole fiber (PBI), it is meant fiber comprising polybibenzimidazole polymer such as made by the processes disclosed in U.S. Patent 2,895,948 and U.S. Reissue 26,065. Polybibenzimidazole 30 fibers can be made by known processes such as those disclosed in U.S. Patent 3,441,640 and U.S. Patent 4,263,245. One useful polybibenzimidazole polymer is poly(2,2'-(m-phenylene)-5,5'-bibenzimidazole) polymer. One commercial PBI polymer is prepared from tetra-aminobiphenyl and diphenyl isophthalate.

By polybenzazole fiber it is meant fiber containing homopolymers and copolymers of polybenzoxazole (PBO), polybenzothiazole (PBT), and polybenzimidazole having a LOI of greater than 21. Suitable polybenzazole homopolymers and copolymers can be made by known
5 procedures, such as those described in U.S. Patents 4,533,693 (to Wolfe et al. on Aug. 6, 1985), 4,703,103 (to Wolfe et al. on Oct. 27, 1987), 5,089,591 (to Gregory et al. on Feb. 18, 1992), 4,772,678 (Sybert et al. on Sept. 20, 1988), 4,847,350 (to Harris et al. on Aug. 11, 1992), and 5,276,128 (to Rosenberg et al. on Jan. 4, 1994). Polybenzimidazoles also
10 include polybenzobisimidazoles; polybenzothiazoles also include polybenzobisthiazoles; and polybenzoxazoles also include polybenzobisoxazoles.

The first fire-resistant fiber of the first flame-resistant fabric has a thermal decomposition temperature that is at least 70 degrees C less than
15 the thermal decomposition temperature of the second fire-resistant fiber of the second flame-resistant fabric. The "thermal decomposition temperature" of the fiber as used herein is the initial major decomposition temperature as determined by ThermoGravimetric Analysis (TGA) in air and is defined as the temperature at the onset point as measured using
20 the modified weight loss (% weight loss/degreeC) scan of the TGA analysis. The onset point is determined by using the TA systems Universal Analysis software program. The onset is defined as the extrapolated beginning point of any transition as determined by the data analysis. Alternatively, this can be shown graphically. The onset point is found by
25 taking the first major derivative peak or shoulder **1** on the derivative weight scan and drawing tangent lines **2** and **3** corresponding to that peak on the modified weight scan as shown on Figure 1, which has scans representative of one embodiment of modacrylic fiber. The intersection of those two tangents provides point **4**, which is the initial major thermal
30 decomposition temperature as defined herein. Likewise, as defined herein, the initial major thermal decomposition temperature of one embodiment of Nomex® meta-aramid fiber is shown via representative scans on Figure 2. Using the first major derivative peak or shoulder **5** on the derivative weight scan, tangent lines **6** and **7** corresponding to that peak are drawn on the

modified weight scan, with the intersection of those two tangents providing the initial major thermal decomposition temperature at point 8. The TGA measurements are made on the TA Systems Q500TGA under default Hi Res conditions (sensitivity 1.0/resolution 4.0). To eliminate the effect of
5 moisture on the analysis, the 100% Y axis is set at 150° C. As measured in this manner, modacrylic has a thermal decomposition temperature of modacrylic is about 225-275° C, while metaphenylene isophthalamide is about 400 to 475° C. The first major derivative peak or shoulder is a deviation in derivative weight from the 0.0 baseline of at least 20 percent.

10 In one embodiment, this invention also relates to a process for making a protective garment having use in a electrical arc potential environment, comprising:

- i) providing a first woven flame-resistant fabric comprising a first fire-resistant fiber made from a synthetic polymer comprising a halogen;
- 15 ii) providing a second woven flame-resistant fabric comprising a second fire-resistant fiber made from a synthetic polymer, wherein the first fire-resistant fiber has a thermal decomposition temperature that is at least 70 degrees C less than the second fire-resistant fiber; the first and second woven flame-resistant fabrics being
20 different;
- iii) combining the first and second woven flame-resistant fabrics to form a arc resistant multilayer fabric laminate, the first and second woven flame-resistant fabrics being distinct fabric layers without any shared weft or warp fabric yarns; and
- 25 iv) forming an arc resistant garment from the arc resistant multilayer fabric laminate wherein the first woven flame-resistant fabric forms an outer surface of the garment and is positioned in the garment closer to the electrical arc potential environment than the second layer.

30 The first and second woven fabrics can be provided in several different ways, including from actual production of the individual yarns using the fiber as previously described in various proportions as previously described, followed by weaving the previously described fabrics from those yarns.

In one preferred embodiment, the individual yarns are made from an intimate blend of staple fibers. By "intimate blend" it is meant the various staple fibers in the composition form a relatively uniform mixture. If desired, other staple fibers can be combined in this relatively uniform mixture of staple fibers. The blending can be achieved by any number of ways known in the art, including processes that creel a number of bobbins of continuous filaments and concurrently cut the two or more types of filaments to form a blend of cut staple fibers; or processes that involve opening bales of different staple fibers and then opening and blending the various fibers in openers, blenders, and cards; or processes that form slivers of various staple fibers which are then further processed to form a mixture, such as in a card to form a sliver of a mixture of fibers. Other processes of making an intimate fiber blend are possible as long as the various types of different fibers are relatively uniformly distributed throughout the blend. The yarns formed from the blend have a relatively uniform mixture of the staple fibers also. Generally, in most preferred embodiments the individual staple fibers are opened or separated to a degree that is normal in fiber processing to make a useful fabric, such that fiber knots or slubs and other major defects due to poor opening of the staple fibers are not present in an amount that detract from the final fabric quality. The yarns can then be combined as previously described herein and woven together on a conventional loom, forming in a preferred embodiment a single layer woven structure of either the first or second woven fabric. The greige fabric can then be finished as desired.

The first and second woven flame-resistant fabrics can then be combined to form an arc resistant multilayer fabric laminate. One convenient method of forming the multilayer fabric laminate is to provide a layer of one of the fabrics on a flat surface, like a cutting table, and then overlay that fabric with a layer of the other fabric. If desired, multiple layers of either the first or second woven flame-resistant fabrics can be used in the multilayer fabric laminate, or one or more layers of flame resistant insulating fabrics, such as those previously described herein, can be laid down or inserted between the first and second flame-resistant fabrics, as

long as they do not detract from the final garment or the desired properties of that garment.

Since the first woven flame-resistant fabric will ultimately form an outer surface of the final garment, care should be taken that when
5 combining the fabrics to form a multilayer fabric laminate, the first woven flame-resistant fabric forms an outer surface of the multilayer fabric laminate. In some embodiments, the second woven flame-resistant fabric forms the opposing outer surface of the multilayer fabric laminate; however, in some other embodiments the opposing outer surface of the
10 multilayer fabric laminate can be another fabric. For example, the opposing outer surface can be a soft fabric that will ultimately be the interior lining of the protective garment, because this multilayer fabric laminate surface will be the interior of the garment and closer to the wearer.

15 The first and second flame-resistant fabrics are combined as separate distinct fabric layers, that is, without any shared weft or warp fabric yarns that might compromise either layer. This allows the first woven flame-resistant fabric to be entirely a sacrificial layer and the second woven flame-resistant fabric to be entirely a thermal protective layer.
20 Further, this provides flexibility to provide additional fabric layers between the first and second flame-resistant fabrics, if desired.

The arc resistant garment is then formed from the arc resistant multilayer fabric laminate. The first woven flame-resistant fabric forms an outer surface of the garment and is positioned in the garment closer to the
25 electrical arc potential environment than the second woven-flame resistant fabric layer when worn.

The garment can be formed by any number of methods; for example, the previously mentioned multilayer fabric laminate can be formed on a cutting table and then the laminate can be cut per a
30 prescribed pattern into fabric shapes suitable for making protective garments such as coats, coveralls, jumpsuits, hoods, etc. Alternatively, such fabric shapes can be obtained by forming the multilayer fabric laminate from individually cut fabric shapes, laying up each layer of fabric as previously described. The multilayer fabric laminate shapes are then

sewn together to form the desired garment with the first flame-resistant fabric of the multilayer fabric laminate forming an outer surface of the final garment, which in use is the exterior of the garment. In so doing, the first woven flame-resistant fabric is positioned in the garment closer to the electrical arc potential environment than the second woven flame-resistant layer.

TEST METHODS

10 ThermGravimetric Analysis (TGA) was conducted in air using ASTM E1131-08 on a TA Instrument Q500 TGA in air from 40-1000° C under TA Systems Hi-Res® with default conditions (sensitivity 1/resolution 4) with a balance gas purge flow of 60 ml/min and a sample gas purge flow of 40 ml/min.

15 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 Arc Thermal Performance Value (ATPV) of each fabric is a measure of the amount of energy that a person wearing that fabric could be exposed to that would be equivalent to a 2nd degree burn from such exposure 50% of the time.

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

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

Basis weight values were obtained according to FTMS 191A; 5041.

EXAMPLES

30

The fabrics used in the following examples were made as follows. Fabric 1 was woven from airjet spun yarn made from an intimate blend of Nomex® type 455 fiber, Kevlar® 29 fiber, and P140 fiber. Nomex® type 455 fiber is non-crystallized poly(m-phenylene isophthalamide)(MPD-I)

staple fiber; Kevlar® 29 fiber is poly(p-phenylene terephthalamide)(PPD-T) staple fiber; and P140 fiber is an antistatic staple fiber having a carbon core and a nylon sheath.

5 A picker blend sliver of 93 wt.% Nomex® type 455 fiber, 5 wt.% Kevlar® 29 fiber, and 2 wt. % P140 fiber was prepared and then processed into spun yarn using a conventional cotton system and an airjet spinning frame. The spun yarn so made was a 15.5 tex (38 cotton count) singles yarn. Two of these singles yarns were then plied together on a plying machine to make a two-ply yarn having a ply twist of 12 turns/inch.

10 The two-ply yarns were then used in both the warp and fill on a shuttle loom to form a plain weave fabric. The greige fabric had a basis weight of 136 g/m² (4.0 oz/yd²). It was scoured in hot water and then jet dyed using basic dye. The finished fabric basis weight was a nominal 153 g/m² (4.5 oz/yd²).

15 Fabric 2 was made in a manner similar to Fabric 1, with the exception that the spun yarn was a 12.2 tex (30 cotton count) single yarn. As in Fabric 1, two of these singles yarns are then plied on the plying machine to make a two-ply yarn having a ply twist of 12 turns/inch. The resulting greige fabric had a basis weight of 186 g/m² (5.5 oz/yd²). It was
20 scoured in hot water and then jet dyed using basic dye. The finished basis weight was a nominal 203 g/m² (6.0 oz/yd²).

Fabric 3 was woven from airjet spun yarn made from an intimate blend of Protex® C fiber, Nomex® type 450 fiber, Kevlar® 29 fiber, and P140 fiber. Protex® C fiber is a modacrylic staple fiber of
25 ACN/polyvinylidene chloride co-polymer with ~10% antimony; Nomex® type 450 fiber is crystallized poly(m-phenylene isophthalamide)(MPD-I) staple fiber; and the Kevlar® 29 fiber and P140 fiber are as in Fabrics 1 and 2. A picker blend sliver of 65 wt. % of Protex® C fiber, 23 wt.% of Nomex® type 450 fiber, 10 wt.% of Kevlar® 29 fiber, and 2 wt. % of
30 antistatic fiber was prepared and then processed into spun yarn in a matter similar to Fabric 1. The spun yarn so made was a 21 tex (28 cotton count) singles yarn. Two of these singles yarns are then plied together on a plying machine to make a two-ply yarn having a ply twist 10turns/inch. The two-ply yarns were then used in both the warp and fill on a shuttle

loom to form a 2x1 twill weave having a construction of 31 ends x 16 picks per cm (77 ends x 47 picks per inch). The greige twill fabric had a basis weight of 203.4 g/m² (6.0 oz/yd²). It was scoured in hot water and then jet dyed using basic dye. The finished twill fabric basis weight was a nominal
5 220.3 g/m² (6.5 oz/yd²).

Fabric 4 was made in a manner similar to Fabric 3, with the exception that the twill fabric had a construction of 31 ends x 28 picks per cm (77 ends x 70 picks per inch). The greige fabric had a basis weight of 254 g/m² (7.5 oz/yd²). After scouring and jet dyeing the fabric had a
10 nominal basis weight of 271 g/m² (8.0 oz/yd²).

Comparative Example A

A multilayer fabric laminate was formed by overlaying Fabric 1 on Fabric 3. To simulate the electrical arc performance of a garment
15 containing this laminate, the laminate was positioned in the arc testing apparatus with Fabric 1 positioned closer to the arc generation point and Fabric 3 closer to an imagined wearer of the garment. This would simulate a garment having Fabric 1 as the outer layer and Fabric 3 as the inner layer. The arc rating this multilayer fabric laminate was then
20 determined and is shown in the Table

Example 1

The multilayer fabric laminate of Comparative Example A was reversed in the arc testing apparatus, with Fabric 3 positioned closer to the
25 arc generation point and Fabric 1 closer to an imagined wearer of the garment. This would simulate a garment having Fabric 3 as the outer layer and Fabric 1 as the inner layer. The arc rating this laminate was then determined and is shown in the Table.

Comparative Example B

Comparative Example A was repeated, except that Fabric 3 was replaced with the heavier Fabric 4. The arc rating this laminate was then determined and is shown in the Table.

Comparative Example C

Comparative Example A was repeated with the exception that Fabric 2 was substituted for Fabric 1. The arc rating this laminate was then determined and is shown in the Table.

5

Example 2

Example 1 was repeated with the exception that Fabric 2 was substituted for Fabric 1. The arc rating this laminate was then determined and is shown in the Table.

10

Table

Example	Outer Fabric	Inner Fabric	Arc Rating (cal / cm²)
A	Fabric 1	Fabric 3	16.7
1	Fabric 3	Fabric 1	28.3
B	Fabric 1	Fabric 4	17.2
C	Fabric 2	Fabric 3	21.3
2	Fabric 3	Fabric 2	32.2

15

20

Example 3

A high arc performance multilayer fabric laminate is formed by overlaying on Fabric 2 three layers of a 1.5 osy Nomex®/Kevlar® spunlaced fabric known as E-89, followed by overlaying with Fabric 4. This forms a multilayer fabric laminate having Fabric 4 as the outer layer and Fabric 2 as the inner layer. This multilayer fabric laminate will provide superior arc performance when used in a garment with the Fabric 4 layer positioned closer to the arc generation point and Fabric 1 closer to an imagined wearer of the garment.

25

30

Example 4

The multilayer fabric laminate of Example 1 is made into a protective garment in the form of a coat, by cutting the multilayer fabric laminates into fabric shapes per a pattern and sewing the shapes together
5 to form a three-quarter length coat. The multilayer fabric laminate of Example 1 is sewn into the coat such that Fabric 3 forms the outer surface layer of the coat and Fabric 1 forms a layer closer to the wearer.

Example 5

10 Example 4 is repeated, but the multilayer fabric laminate of Example 3 is used and it is positioned in the coat such that Fabric 4 forms the outer surface layer of the coat and Fabric 1 forms a layer closer to the wearer. In addition, a light cotton lining fabric is used to line the inside of the coat and is positioned between the wearer and Fabric 1.

15

Example 6

The multilayer fabric laminates of Examples 1, 2, & 3 are used to make various protective garments, including coveralls, jumpsuits, and hoods. In each garment the previously designated multilayer fabric
20 laminate outer layer (Fabrics 3, 3, & 4, respectively) forms the outer surface layer of the garments.

CLAIMS

What is claimed is:

- 5 1. A protective garment having use in a electrical arc potential environment, the garment having an arc resistant multilayer fabric laminate comprising:
- 10 i) a first layer of a woven flame-resistant fabric forming an outer surface of the garment and comprising a first fire-resistant fiber made from a synthetic polymer comprising a halogen; and
- 15 ii) a second layer of a woven flame-resistant fabric comprising a second fire-resistant fiber made from a synthetic polymer; wherein the first fire-resistant fiber has a thermal decomposition temperature that is at least 70 degrees C less than the second fire-resistant fiber; and
- 20 wherein the fabrics in the first and second layers are different and the first layer is positioned in the garment to be closer the electrical arc potential environment than the second layer.
- 25 2. The protective garment of claim 1, wherein the first fire-resistant fiber is present in the woven fabric of the first layer in an amount of at least 20 percent by weight.
- 30 3. The protective garment of claim 2, wherein the halogen is chlorine.
4. The protective garment of claim 3, wherein the first fire-resistant fiber is modacrylic.
5. The protective garment of claim 1, wherein the woven flame-resistant fabric of the second layer comprises aramid fiber, polybibenzimidazole fiber, or polybenzazole fiber, or a blend of any of these fibers.

6. The protective garment of claim 1, wherein the first layer is in direct contact with the second layer.
7. The protective garment of claim 1, wherein the woven flame-resistant fabric of the first layer and the woven flame-resistant fabric of the second layer are distinct fabric layers without any shared weft or warp fabric yarns.
8. The protective garment of claim 1 further comprising 1 to 4 layers of an 0.5 to 3.0 oz/yd² insulating fabric positioned between the first and second flame-resistant fabric.
9. A process for making a protective garment having use in a electrical arc potential environment, comprising:
- i) providing a first woven flame-resistant fabric comprising a first fire-resistant fiber made from a synthetic polymer comprising a halogen;
 - ii) providing a second woven flame-resistant fabric comprising a second fire-resistant fiber made from a synthetic polymer, wherein the first fire-resistant fiber has a thermal decomposition temperature that is at least 70 degrees C less than the second fire-resistant fiber; the first and second woven flame-resistant fabrics being different;
 - iii) combining the first and second woven flame-resistant fabrics to form a arc resistant multilayer fabric laminate, the first and second woven flame-resistant fabrics being distinct fabric layers without any shared weft or warp fabric yarns; and
 - iv) forming an arc resistant garment from the arc resistant multilayer fabric laminate wherein the first woven flame-resistant fabric is positioned in the garment closer to the electrical arc potential environment than the second layer.

10. The process for making an arc resistant garment of claim 9, wherein the first fire-resistant fiber is modacrylic.
11. The process for making an arc resistant garment of claim 9, wherein the second woven flame-resistant fabric comprises aramid fiber, polybibenzimidazole fiber, or polybenzazole fiber, or a blend of any of these fibers.
12. The process for making an arc resistant garment of claim 9 further comprising positioning 1 to 4 layers of an 0.5 to 3.0 oz/yd² insulating fabric between the first and second woven flame-resistant fabric layers in step iii).

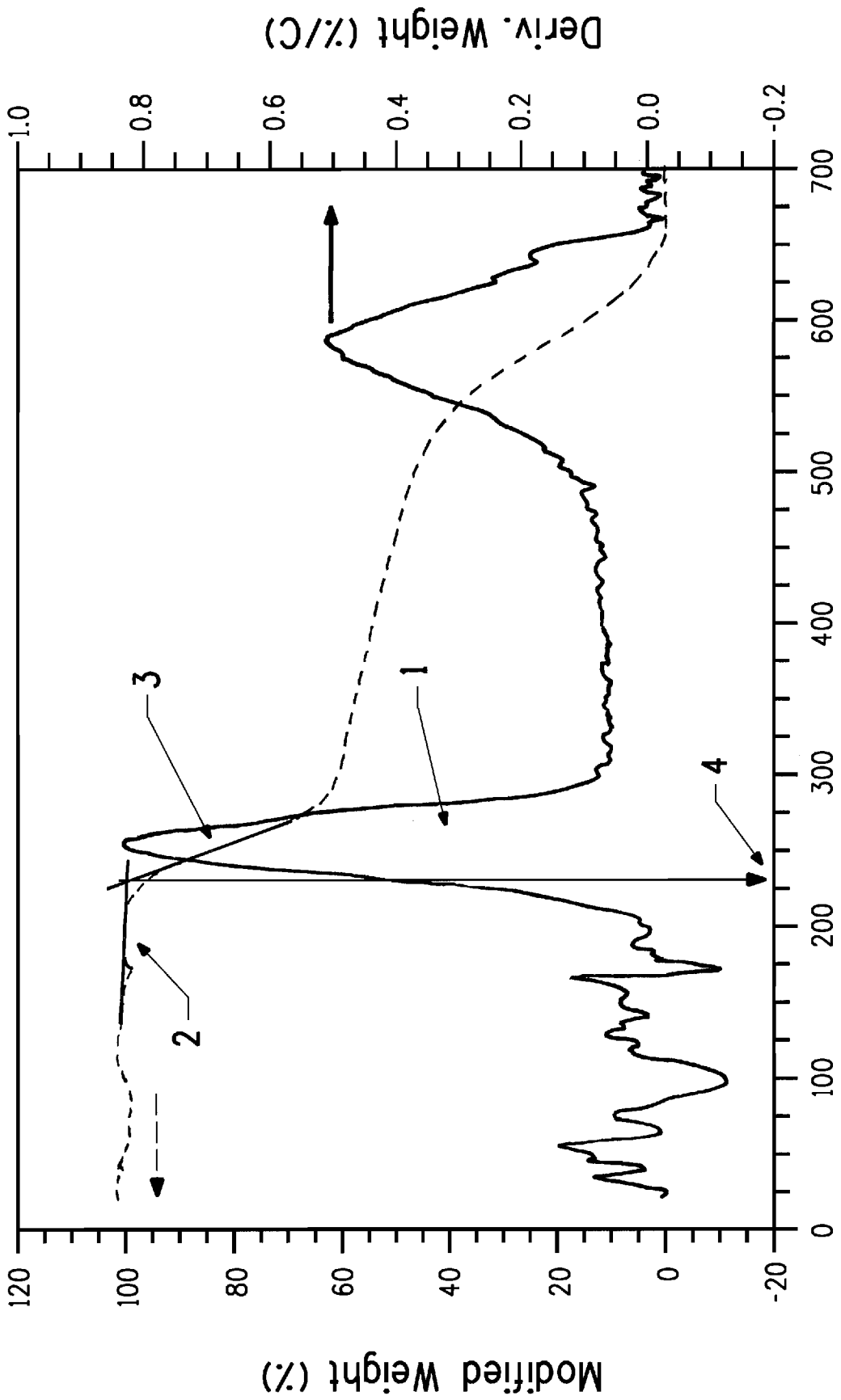


FIG. 1

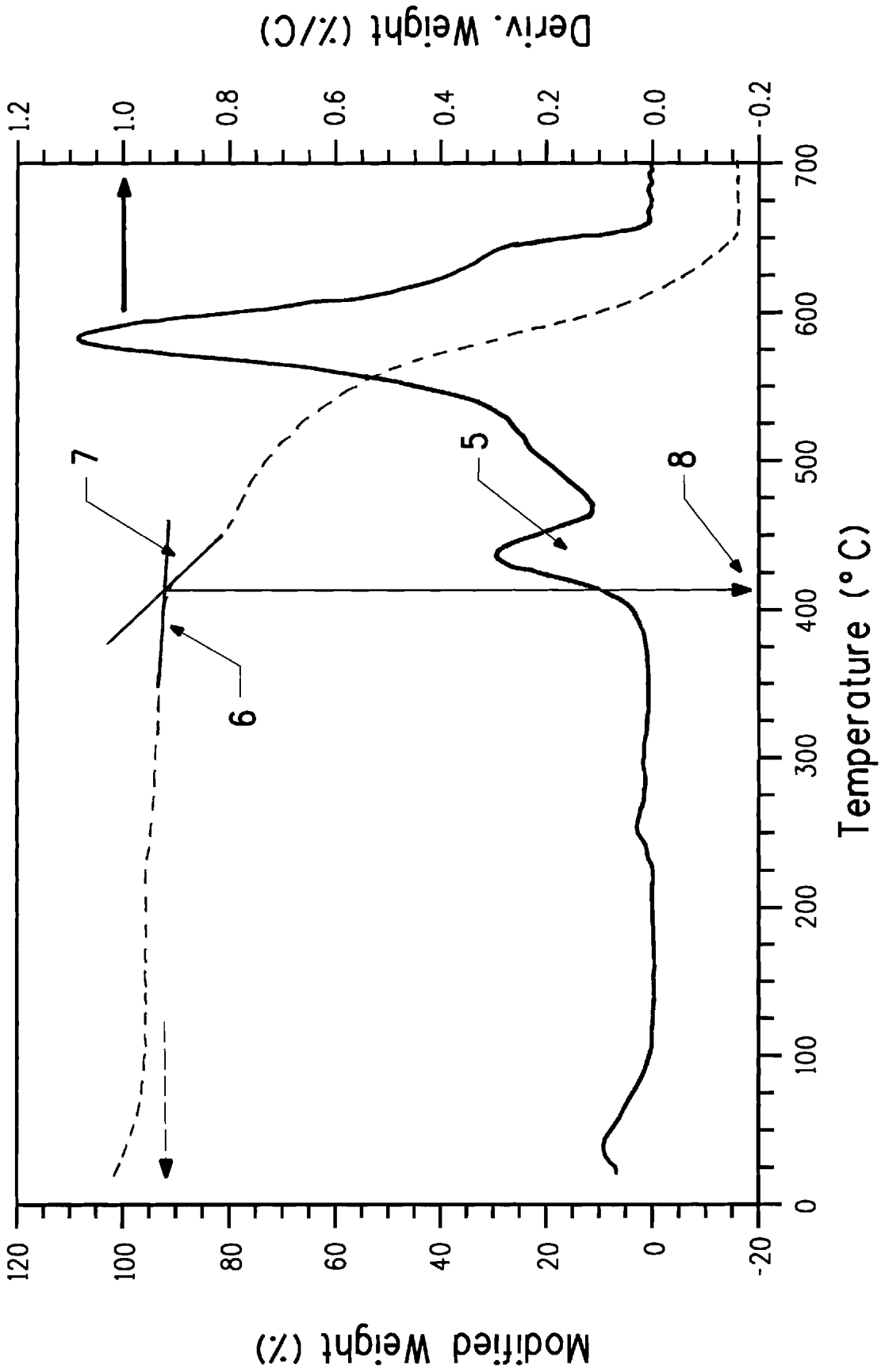


FIG. 2