

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 June 2011 (03.06.2011)

(10) International Publication Number
WO 2011/066308 A2

PCT

(51) International Patent Classification:

D06B 3/10 (2006.01) **D06M 11/45** (2006.01)
D06B 3/04 (2006.01) **D06M 11/77** (2006.01)
D06M 11/49 (2006.01) **D06M 11/83** (2006.01)

(21) International Application Number:

PCT/US2010/057854

(22) International Filing Date:

23 November 2010 (23.11.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12/627,911 30 November 2009 (30.11.2009) 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, 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, PE, PG, PH, PL, PT, RO, RS, RU, 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, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, 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:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: METHOD OF PROTECTING A PERSON FROM HOT HIGH HEAT CAPACITY MATERIALS AND HOT CORROSIVE MATERIALS

(57) Abstract: Methods of protecting a person, animal or other object from hot high heat capacity and/or hot corrosive materials, such as hot molten metal, hot oily liquids (e.g., heating oil), hot gels, hot solids, hot sparks, and hot acids. The methods include protecting a person, animal or other object from hot molten metals, such as liquid metal zinc heated to a temperature of about 950 °F (510 °C) or greater, hot molten aluminum heated to a temperature of about 1150 °F (620 °C) or greater, burning phosphorus at temperature of about 1550 °F (843 °C) or greater, hot solid iron having a temperature of about 500 °F (260 °C) or greater, hot heating oil having a temperature of about 500 °F (260 °C) or greater, and hot hydrochloric acid having a temperature of about 300 °F (150 °C) or greater. The ability to protect a wearer from heat from hot high heat capacity materials and/or hot corrosive materials is quite different from simply shedding liquids, even flammable liquids, such as gasoline is unexpected.



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**METHODS OF PROTECTING A PERSON FROM HOT HIGH HEAT
CAPACITY MATERIALS AND HOT CORROSIVE MATERIALS**

BACKGROUND OF THE INVENTION

1. The Field of the Invention

5 The present invention is in the field of heat and corrosive material blocking fabrics and methods of protecting an object from the effects of heat caused by hot heat capacity materials, such as molten metals, hot oily liquids, hot gels, hot solids, or hot sparks, and also hot corrosive materials, such as hot acids.

2. The Relevant Technology

10 Fire retardant clothing is widely used to protect persons who are exposed to fire, particularly suddenly occurring and fast burning conflagrations. These include persons in diverse fields, such as race car drivers, military personnel, fire fighters, and metal workers, each of which may be exposed to deadly fires, heat, and extremely dangerous incendiary conditions. For such persons, the primary line of defense
15 against severe burns and even death is the protective clothing worn over some or all of the body.

 Even though fire retardant clothing presently exists, such clothing is not always adequate to reliably offset the risk of severe burns, or even death. This is particularly true in the case where a person is not only exposed to flame or high heat
20 but contacted with hot substances, such as a hot molten metal, hot oily liquid, hot gel, hot solid, hot sparks, or hot acid. For example, splashing of sparks and molten metal could occur, for example, in the case of welders and steel or other metal workers who routinely handle molten metal as it is poured and otherwise transported to manufacture finished steel and other metal products.

25 Flammable fabrics such as cotton, linen, wool, silk, polyester, rayon, polyamides, cellulose acetate, and regenerated cellulose have been treated with a fire retardant finish to enhance fire retardance. While this may temporarily increase the flame retardant properties of such fabrics, typical fire retardant finishes are not permanent. Exposure of the treated fabric to UV radiation (*e.g.*, sun light) as well as
30 routine laundering of the fabric can greatly reduce the fire retardant properties of the fabric. The user may then have a false sense of security, thus unknowingly exposing himself to increased risk of burns. There may be no objective way to determine, short

of being caught in a fiery conflagration or similarly dangerous environment, whether a treated garment still possesses sufficient fire retardance to offset the risks to which the wearer may be exposed.

The foregoing fabrics have also been coated with silicone polymers to render them permanently highly water repellant as in U.S. Patent No. 5,004,643 to Caldwell. However, such fabrics provide no protection to a wearer exposed to hot high heat capacity materials, such as hot molten metal, hot liquids, hot gels, hot solids, or hot sparks, or hot corrosive materials, such as hot acids.

U.S. Patent Nos. 6,287,686 and 6,358,608 to Huang et al. disclose a range of yarns and fabrics that preferably include about 85.5-99.9% by weight oxidized polyacrylonitrile ("O-Pan") fibers and about 0.1-14.5% by weight of one or more strengthening fibers. U.S. Patent No. 4,865,906 to Smith, Jr. includes about 25-85% O-Pan fibers combined with at least two types of strengthening fibers. Flame retardant and heat resistant fabrics made according to the Huang et al. patents are sold under the name CARBONX by Chapman Thermal Products, Inc., located in Salt lake City, Utah. Such fabrics, however, have been shown to be vulnerable to charring and irreparable damage when exposed to hot molten metal, and other hot high heat capacity materials or hot corrosive materials, thus offering little protection to a person exposed to hot high heat capacity materials, such as hot molten metal, hot liquids, hot gels, hot solids, or hot sparks, or hot corrosive materials, such as hot acids.

BRIEF SUMMARY OF THE INVENTION

The present invention encompasses methods of protecting a person, animal or other object from the effects of hot high heat capacity and/or hot corrosive materials, such as hot molten metal, hot oily liquids (*e.g.*, heating oil), hot gels, hot solids, hot sparks, and hot acids. It has unexpectedly been found that fabrics made from O-Pan or other high LOI materials and in which the yarn strands are encapsulated with a silicone polymer or other liquid shedding material (*e.g.*, according to U.S. Patent Publication No. 2007/0231573) not only shed flammable liquids but can also protect a wearer from the effects of hot high heat capacity materials, such as molten metal, hot oily liquids, hot gels, hot solids, and hot sparks and/or hot corrosive materials, such as hot acids. A user can be protected against receiving second and third degree burns when exposed to such materials.

The inventive methods include protecting a person, animal or other object from hot molten metals, such as liquid metal zinc heated to a temperature of about 950 °F (510 °C) or greater, hot molten aluminum heated to a temperature of about 1150 °F (620 °C) or greater, burning phosphorus at temperature of about 1550 °F (843 °C) or greater, hot solid iron having a temperature of about 500 °F (260 °C) or greater, hot heating oil having a temperature of about 500 °F (260 °C) or greater, and hot hydrochloric acid having a temperature of about 300 °F (150 °C) or greater. The ability to protect a wearer from heat from hot high heat capacity materials and/or hot corrosive materials is quite different from simply shedding liquids, even flammable liquids, such as gasoline and is an unexpected result.

These and other advantages and features of the present invention will become more fully apparent from the following description and appended claims, or may be learned by the practice of the invention as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

In order that the manner in which the above recited and other benefits, advantages and features of the invention are obtained, a more particular description of the invention briefly described above will be rendered by reference to specific embodiments thereof which are illustrated in the appended drawings. Understanding that these drawings depict only typical embodiments of the invention and are not therefore to be considered limiting of its scope, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

Figure 1 is a perspective view of the testing apparatus used to evaluate heat transfer characteristics of a sample of fabric to be evaluated;

Figure 2 is a perspective view of the testing apparatus of Figure 1 with molten iron being poured onto the sample fabric;

Figure 3 is a schematic side view of the testing apparatus of Figure 2;

Figure 4A is a graph showing temperature rise as a function of time while testing an O-Pan based fabric that is not coated or encapsulated in silicone;

Figure 4B is a graph showing total heat energy transfer as a function of time of the same O-Pan based fabric evaluated in Figure 4A;

Figure 5A is a graph showing temperature rise as a function of time while testing an O-Pan based fabric that is encapsulated in silicone; and

Figure 5B is a graph showing total heat energy transfer as a function of time of the same silicone encapsulated O-Pan based fabric evaluated in Figure 5A.

5 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

I. INTRODUCTION AND DEFINITIONS

 The present invention encompasses methods of protecting a person, animal or other object from the effects of hot high heat capacity and/or hot corrosive materials, such as hot molten metal, hot oily liquids (*e.g.*, heating oil), hot gels, hot solids, hot sparks, and hot acids. It has unexpectedly been found that fabrics made from O-Pan or other high LOI materials and in which the yarn strands are encapsulated with a liquid-shedding silicone polymer or other liquid shedding material (*e.g.*, according to U.S. Patent Publication No. 2007/0231573) not only shed flammable liquids but can also protect a wearer from the effects of hot heat capacity materials, such as molten metal, hot liquids, hot gels, hot solids, and hot sparks and/or hot corrosive materials, such as hot acids. A user can be protected against receiving second and third degree burns when exposed to such materials.

 The inventive methods include protecting a person, animal or other object from hot molten metals, such as liquid metal zinc heated to a temperature of about 950 °F (510 °C) or greater, hot molten aluminum heated to a temperature of about 1150 °F (620 °C) or greater, burning phosphorus at temperature of about 1550 °F (843 °C) or greater, hot solid iron having a temperature of about 500 °F (260 °C) or greater, hot heating oil having a temperature of about 500 °F (260 °C) or greater, and hot hydrochloric acid having a temperature of about 300 °F (150 °C) or greater. The ability to protect a wearer from heat from hot high heat capacity materials and/or hot corrosive materials is quite different from simply shedding liquids, even flammable liquids, such as gasoline and is an unexpected result.

 According to various example embodiments, methods are provided for protecting an object exposed to a hot high heat capacity material and/or hot corrosive material having a temperature of at least about 300 °F (150 °C), or a temperature of at least about 400 °F (200 °C), or a temperature of at least about 500 °F (260 °C), or a temperature of at least about 600 °F (315 °C), or a temperature of at least about 750

°F (400 °C), or a temperature of at least about 950 °F (510 °C), or a temperature of at least about 1150 °F (620 °C).

The protective fire fabrics includes utilized in the inventive methods include yarn coated or encapsulated by a liquid/gel/spark/molten metal-resistant and strengthening coating to yield fabrics and articles that provide better tensile strength, abrasion resistance, durability, and the ability to protect a wearer from hot heat capacity materials, such as hot molten metals, hot oily liquids, hot gels, hot solid metals, hot sparks, and hot corrosive materials, such as hot acids. Coating or encapsulating the individual yarn strands (*i.e.*, so as to maintain empty space between individual strands), rather than coating and plugging the whole fabric (*i.e.*, in which space between strands is plugged with polymer and strands become glued together), not only seals the individual yarn strands in superior fashion, it also maintains breathability of the fabric.

The term “Limiting Oxygen Index” (or “LOI”) is defined as the minimum concentration of oxygen necessary to support combustion of a material. The LOI is primarily a measurement of flame retardancy rather than temperature resistance. Temperature resistance is typically measured as the “continuous operating temperature”.

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

The term “abrasion resistance” refers to the tendency of a fabric to resist fraying and thinning during normal wear. Although related to tensile strength, abrasion resistance also relates to other measurements of yarn strength, such as shear strength and modulus of elasticity, as well as the tightness and type of the weave or knit.

The terms “fiber” and “fibers” refers to any slender, elongated structure that can be carded or otherwise formed into a thread. Fibers typically have a length of about 2 mm to about 75 mm and an aspect ratio of at least about 100:1. Examples include “staple fibers”, a term that is well-known in the textile art. The term “fiber”
5 differs from the term “filament”, which is defined separately below and which comprises a different component of the inventive yarns.

The term “thread”, as used in the specification and appended claims, shall refer to continuous or discontinuous elongated strands formed by carding or otherwise joining together one or more different kinds of fibers.

10 The term “filament” shall refer to a thread of indefinite length, whether comprising multiple fibers or a monofilament.

The term “yarn” shall refer to a continuous strand comprised of a multiplicity of fibers, filaments, or the like in bundled form, such as may be suitable for knitting, weaving or otherwise used to form a fabric.

15 The term “fabric” shall refer to an article of manufacture formed by knitting, weaving or otherwise joining a plurality of yarn strands together to form a multi-dimensional structure used to manufacture a wide variety of useful articles.

The terms “coat”, “outer layer”, “encapsulate” and “outer shell” shall refer to the positioning or placement of a liquid-shedding, spark-shedding, and molten metal-shedding polymer material over or around an inner core comprising a yarn strand,
20 before or after the yarn is formed into a fabric. The terms “coat”, “outer layer”, “encapsulate” and “outer shell” refer to the fact that at least some of the liquid/gel/spark/molten metal-shedding polymer material is located on an outer perimeter of the yarn strand(s). They do not mean that some of the liquid/gel/spark/molten metal-shedding polymer material that “coats” or
25 “encapsulates” the inner yarn core cannot also be located in interstitial spaces or pores within the inner yarn core. According to some embodiments, the polymer material may only coat one side of a fabric (*e.g.*, as accomplished by knife coating) rather than coating both sides so as to encapsulate the fabric with an outer shell. The terms
30 “coat” and “outer layer” describe such embodiments. In single side coated embodiments, the coated outer layer surface becomes the exterior of the article of manufacture, so that when the coated surface is contacted by any liquids, gels, sparks,

or molten metal, the fabric is able to shed these materials, protecting the wearer. The uncoated surface is inwardly oriented so as to contact the wearer's body or underclothes.

The term "inner core" shall refer to the fire retardant and heat resistant yarn that is coated or encapsulated by the liquid/gel/spark/molten metal-resistant and strengthening polymer.

II. PROTECTIVE FABRICS

Fire retardant and heat resistant yarns used to make protective fabrics according to the invention comprise at least one type of fire retardant and heat resistant fibers and/or filaments, preferably combined or blended with at least one type of strengthening fibers and/or filaments. Fire retardant and heat resistant fibers can be carded into a yarn, either alone or in combination with one or more types of strengthening fibers. Multiple yarns can be twisted or braided together to form a larger yarn strand. One or more fire retardant and heat resistant yarns comprising mainly or solely fire retardant and heat resistant fibers or filament(s) can be twisted or braided together with one or more strengthening strands comprising mainly or solely strengthening fibers and/or filament(s). Because a yarn strand typically consists of multiple strands twisted or braided together, it will typically include a substantial amount of interstitial space between the individual strands, at least before being coated or encapsulated by the liquid/gel/spark/molten metal-shedding polymer.

Fabrics comprising the fire retardant and heat resistant yarns can be formed by knitting, weaving or otherwise combining multiple strands of yarn together. Any known method of forming a fabric from a yarn can be utilized to form the inventive fire retardant and heat resistant fabrics. Exemplary fire retardant and heat resistant yarns, fabrics and articles that can be improved according to the present invention are disclosed in U.S. Patent Nos. 6,287,686, 6,358,608, 6,800,367 and 4,865,906.

A. Fire Retardant and Heat Resistant Fibers and Filaments

Exemplary fire retardant and heat resistant fibers and filaments are made from oxidized polyacrylonitrile (O-Pan). The O-Pan fibers or filaments within the scope of the invention may comprise any type of O-Pan having high fire retardance and heat resistance. In a preferred embodiment, O-Pan is obtained by heating polyacrylonitrile (*e.g.*, polyacrylonitrile fibers or filaments) in a cooking process between about 180°C

to about 3000°C for at least about 120 minutes. This heating/oxidation process is where the polyacrylonitrile receives its initial carbonization. Preferred O-Pan fibers and filaments have an LOI of about 50-65. In most cases, O-Pan made in this way may be considered to be nonflammable.

5 Examples of suitable O-Pan fibers include LASTAN, manufactured by Ashia Chemical in Japan; PYROMEX, manufactured by Toho Rayon in Japan; PANOX, manufactured by SGL; and PYRON, manufactured by Zoltek. It is also within the scope of the invention to utilize filaments that comprise O-Pan. It was heretofore believed that fabrics that include a substantial amount of O-Pan fibers and/or
10 filaments will resist burning and charring, even when exposed to intense heat or flame exceeding 3000°F. However, it has now been learned that O-Pan containing fabrics that include unencapsulated and unprotected yarns can, in fact, become charred and become irreparable damaged when exposed to hot molten metals and other high heat capacity materials.

15 Other fire retardant and heat resistant materials can be used in addition to, or in place of, O-Pan so long as they have fire retardant and heat resistance properties that are comparable to those of O-Pan. By way of example, polymers or other materials having an LOI of at least about 50 and which do not burn when exposed to heat or flame having a temperature of about 3000°F could be used in addition to, or
20 instead of, O-Pan.

 The fire retardant and heat resistant yarn comprising the fabric portion of the protective article may consist solely of O-Pan fibers or filaments. When the O-Pan is blended with one or more strengthening fibers or filaments, O-Pan is preferably included in an amount in a range of about 25% to about 99.9% by weight of the fabric
25 or yarn (exclusive of the polymer coating), more preferably in a range of about 40% to about 95% by weight, and most preferably in a range of about 50% to about 90% by weight of the fabric or yarn (exclusive of the polymer coating).

B. Strengthening Fibers and Filaments

 Strengthening fibers and filaments that may be incorporated into fire retardant
30 and heat resistant yarns, fabrics and articles of the present invention may comprise any fiber or filament known in the art. In general, preferred strengthening fibers will be those that have a relatively high LOI and TPP compared to natural organic fibers

such as cotton, although the use of such fibers is within the scope of the invention. The strengthening fibers preferably have an LOI greater than about 20.

Strengthening fibers may be carded or otherwise formed into yarn, either alone or in combination with other fibers (*e.g.*, O-Pan fibers). Strengthening yarns or
5 filaments may be twisted, braided or otherwise combined with fire retardant and heat resistant strands to form a blended yarn.

Strengthening fibers and filaments within the scope of the invention include, but are not limited to, polybenzimidazole (PBI), polybenzoxazole (PBO), polyphenylene-2,6-benzobisoxazole (PBO), modacrylic, p-aramid, m-aramid,
10 polyvinyl halides, wool, fire resistant polyesters, fire resistant nylons, fire resistant rayons, cotton, linen, and melamine. By way of comparison with O-Pan, which has an LOI of about 50-65, the LOI's of selected strengthening fibers are as follows:

	PBO	68
	PBI	35-36
15	modacrylic	28-32
	m-Aramid	28-36
	p-Aramid	27-36
	wool	23
	polyester	22-23
20	nylon	22-23
	rayon	16-17
	cotton	16-17

Examples of suitable p-aramids include KEVLAR, manufactured by DuPont; TWARON, manufactured by Twaron Products BB; and TECHNORA, manufactured
25 by Teijin. Examples of suitable m-aramids include NOMEX, manufactured by DuPont; CONEX, manufactured by Teijin; and P84, an m-aramid yarn with a multi-lobal cross-section made by a patented spinning method, manufactured by Inspec Fiber. For this reason P84 has better fire retardant properties as compared to NOMEX.

30 An example of a PBO is ZYLON, manufactured by Toyobo. An example of a PBI fiber is CELAZOLE of PBI Performance Products, Inc. An example of a

melamine fiber is BASOFIL. An example of a fire retardant or treated cotton is PROBAN, manufactured by Westex. Another is FIREWEAR.

Strengthening fibers and filaments may be incorporated in the yarns of the present invention in at least the following ways: (1) as one or more strengthening
5 filaments twisted, wrapped, braided or otherwise joined together with threads or filaments comprising oxidized polyacrylonitrile; or (2) as fibers blended with O-Pan fibers into one or more yarns.

In short, strengthening fibers may be added to the inventive yarns in the form of strengthening yarns comprising one or more different types of strengthening fibers,
10 a blended yarn comprising O-Pan fibers and one or more different types of strengthening fibers, or as a strengthening filament. When O-Pan is blended with one or more strengthening fibers or filaments, the strengthening fibers or filaments are preferably included in an amount in a range of about 0.1% to about 75% by weight of the fabric or yarn (exclusive of the polymer coating), more preferably in a range of
15 about 5% to about 60% by weight, and most preferably in a range of about 10% to about 50% by weight of fabric or yarn (exclusive of the polymer coating).

C. Metallic and Ceramic Filaments

Yarns according to the invention may include one or more types of metallic or ceramic filaments in order to increase cut resistance, tensile strength and abrasion
20 resistance. Metallic filaments typically have the highest combination of tensile strength and cut resistance but also conduct heat more rapidly. Examples of metals used to form high strength filaments include, but are not limited to, stainless steel, stainless steel alloys, other steel alloys, titanium, aluminum, copper, and the like.

Examples of high strength ceramic filaments include silicon carbide, graphite,
25 silica, aluminum oxide, other metal oxides, and the like. Examples of high strength and heat resistant ceramic filaments are set forth in U.S. Patent Nos. 5,569,629 and 5,585,312 to TenEyck et al., which disclose ceramic filaments that include 62-85% by weight SiO_2 , 5-20% by weight Al_2O_3 , 5-15% by weight MgO , 0.5-5% by weight TiO_x , and 0-5% ZrO_2 . High strength and flexible ceramic filaments based on a blend
30 of one or more oxides of Al, Zr, Ti, Si, Fe, Co, Ca, Nb, Pb, Mg, Sr, Cu, Bi and Mn are disclosed in U.S. Patent No. 5,605,870 to Strom-Olsen et al. For purposes of

disclosing high strength ceramic filaments, the foregoing patents are incorporated herein by reference. Fiberglass filaments can also be used.

Strengthening filaments preferably have a diameter in a range of about 0.0001" to about 0.01", more preferably in a range of about 0.0005" to about 0.008",
5 and most preferably in a range of about 0.001" to about 0.006". Yarns containing a high concentration of oxidized polyacrylonitrile fibers that are generally too weak to be used in the manufacture of fire retardant and heat resistant fabrics can be greatly strengthened with even small percentages of one or more metallic filaments, and fabrics manufactured therefrom have been found to be surprisingly strong.

10 In general, where it is desired to maximize the strength of the material, it will be preferable to maximize the volume of strengthening filaments that are added to the yarn. However, it will be appreciated that as the amount of strengthening filaments increases in the yarn, the heat resistance generally declines. As a practical matter, the fire retardant and heat resistant requirements of the resulting yarn, fabric or other
15 fibrous blend will determine the maximum amount of strengthening filaments that can be added to the yarn.

D. Encapsulation of Yarns

The fire retardant and heat resistant yarns and fabrics discussed above can be treated according to the invention by coating or encapsulating the yarn with a liquid
20 shedding and strengthening polymer coating. Exemplary liquid-shedding and strengthening polymer materials, optional compositions applied to yarns in addition to the liquid shedding and strengthening polymer materials, as well as methods for coating or encapsulating yarns with the liquid shedding and strengthening polymer materials, are disclosed in U.S. Patent Nos. 4,666,765, 5,004,643, 5,209,965,
25 5,418,051, 5,856,245, 5,869,172, 5,935,637, 6,040,251, 6,071,602, 6,083,602, 6,129,978, 6,289,841, 6,312,523, 6,342,280 and 6,416,613. It should be understood, however, that materials disclosed in these patents are merely liquid-shedding and cannot by themselves render conventional fabrics protective against hot heat capacity and/or hot corrosive materials. It is the unexpected and unpredictable synergy
30 between such materials and the disclosed protective fabrics that results in protection to a wearer against the effects of hot high heat capacity materials and/or hot corrosive materials.

Exemplary liquid-shedding and strengthening polymer coatings include a wide variety of curable silicone-based polymers and polysiloxanes. Such polymers are typically applied as an uncured or partially cured polymer resin and then cured (*i.e.*, cross-linked and/or further polymerized) after coating or encapsulating the yarn being
5 treated. The polymer resins before application typically have a viscosity in a range of about 1000 cps to about 2,000,000 cps at a shear rate of 1/10s and a temperature of 25°C. The polymer resins preferably have a viscosity in a range of about 5000 cps to about 10,000 cps at a shear rate of 1/10s and a temperature of 25°C. In a most preferred embodiment, such polymer resins preferably contain less than about 1% by
10 weight of volatile material. When cured, the coating or encapsulating polymers are preferably elastomeric in order to yield a generally flexible yarn, fabric or article.

A preferred class of liquid curable silicone polymer compositions comprises a curable mixture of the following components: (1) at least one organo-hydrosilane polymer or copolymer; (2) at least one vinyl substituted polysiloxane polymer or
15 copolymer; (3) a platinum or platinum containing catalyst; and (4) optionally fillers and additives.

Typical silicone hydrides (component 1) are polymethylhydrosiloxanes which are dimethyl siloxane copolymers. Typical vinyl terminated siloxanes are vinyl-dimethyl terminated or vinyl substituted polydimethyl siloxanes. Typical catalyst
20 systems include solutions or complexes of chloroplatinic acid in alcohols, ethers, divinylsiloxanes, and cyclic vinyl siloxanes.

Particulate fillers can be included to extend and reinforce the cured polymer composition and also improve the thixotropic behavior of the uncured polymer resins.

Exemplary silicone polymer resins that may be used to coat or encapsulate fire
25 retardant and heat resistant yarns according to the invention include, but are not limited to, SILOPREN LSR 2530 and SILOPREN LSR 2540/01, which comprise a vinyl-terminated polydimethyl/siloxane with fumed silica and methylhydrogen siloxane, which are available from Mobay Chemical Co.; SILASTIC 595 LSR, a polysiloxane available from Dow Corning; SLE 5100, SLE 5110, SLE 5300, SLE
30 5500, and SLE 6108, which are polysiloxanes, and SLE 5106, a siloxane resin solution, all available from General Electric; KE 1917 and DI 1940-30, silicone

polymers available from Shin-Etsu; LIQUID RUBBER BC-10, a silicone fluid with silicone dioxide filler and curing agents, available from SWS Silicones Corporation.

The foregoing silicone polymer resins are characterized as having high viscosity. Depending on the method of coating or encapsulation, in order for such
5 polymer resins to properly coat or encapsulate the yarn, they may typically be thinned in some manner to reduce the viscosity so as to flow around the yarn and at least partially penetrate into the interstitial spaces within the yarn. This may be accomplished in any desired manner. According to one embodiment, the polymer resins are subjected to high shearing conditions, which causes them to undergo shear
10 thinning and/or thixotropic thinning. Any suitable mixing blade, combination of blades, or other apparatus capable of applying high shear may be introduced into the vessel containing the polymer resin in order to temporarily reduce the viscosity of the resin before or during application to the yarn or fabric.

According to one method, such polymers may be encapsulated over the
15 individual yarn strands of a tensioned fabric that is drawn through a bath of shear and/or thixotropically thinned polymer resin. Thereafter, the polymer resin is cured to form the final encapsulated yarn. Curing may be carried out using heat to accelerate polymerization and/or cross-linking of the polymer resin. The process advantageously only encapsulates the yarn strands but leaves spaces between the yarn
20 strands that are woven or knitted together so as to permit the treated fabric to breathe. In this way, the treated fabric still feels and behaves more like an ordinary fabric rather than a laminate sheet or plugged fabric.

As an alternative to the above described encapsulation method in which the yarn or fabric is drawn through a bath of shear thinned polymer composition, the
25 shedding polymer composition may be applied by a knife coating method. Generally speaking, in a knife coating method the uncured polymer composition is applied to the tensioned fabric, which then passes through a gap between a knife and a support roller. As the tensioned fabric substrate passes through the gap, the excess polymer composition is scraped off by the knife, further ensuring that the uncured polymer
30 composition is evenly spread over individual yarns, resulting in proper coating. Because the fabric is under tension, the exposed surface of the individual yarn strands are coated, but spaces between yarn strands are not, so as to permit the treated fabric

to breath and feel more like an ordinary fabric rather than a plugged fabric. Such a method may be used to coat only one side of a fabric. Of course, in embodiments where only one side of a fabric is coated, the coated side of the fabric becomes the protected exterior surface of the article of manufacture made from the fabric which exhibits the shedding ability, so that the exterior surface of the article is able to shed liquids, gels, sparks and molten metal. Preferably, both sides of the fabric are coated. In order to completely encapsulate the fabric substrate, the fabric may be processed again so as to coat the opposing surface of the fabric. It may also be possible to operate multiple knives simultaneously so as to coat both sides of a fabric in a single operation

According to one embodiment, the silicone polymer resin is blended with a benzophenone (*e.g.*, about 0.3-10 parts by weight of the silicone polymer), examples of which include 2,4-dihydroxybenzophenone (*e.g.*, UVINUL 400, available from BASF), 2-hydroxy-4-methoxybenzophenone (*e.g.*, UVINUL M-40, available from BASF), 2,2',4,4'-tetrahydroxybenzophenone (*e.g.*, UVINUL D-50, available from BASF), 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (*e.g.*, UVINUL D-49, available from BASF), mixed tetra-substituted benzophenones (*e.g.*, UVINUL 49 D, available from BASF), and 2-ethylhexyl-2-cyano-3,3-diphenylacrylate (*e.g.*, UVINUL N-539, available from BASF).

The silicone polymer resin may also be blended with an accelerator (*e.g.*, Dow Corning 7127 accelerator, a proprietary polysiloxane material) (*e.g.*, 5-10 parts by weight of the silicone polymer resin) just before being applied to the yarn or fabric to promote curing.

The silicone polymer resin may further include various additives in order to impart desired properties to the yarn or fabric. Exemplary additives include UV absorbers, flame retardants, aluminum hydroxide, filling agents, blood repellants, flattening agents, optical reflective agents, hand altering agents, biocompatible proteins, hydrolyzed silk, and agents that affect thermal conductivity, radiation reflectivity, and/or electrical conductivity.

In general, the yarn is typically coated or encapsulated with the liquid, spark, and molten metal-resistant coating after being woven or knitted into a fabric. Nevertheless, it is within the scope of the invention to coat or encapsulate the yarn

before forming it into a fabric. One or more individual yarn strands can be encapsulated by drawing them through a bath of shear thinned polymer composition and then curing the polymer. The treated yarn strands may then be knitted, woven or otherwise joined together to form a desired fabric.

5 The silicone polymer coating is preferably applied to the yarn or fabric in an amount in a range of about 5% to about 200% by weight of the original yarn or fabric, more preferably in an amount in a range of about 10% to about 100% by weight of the original yarn or fabric.

 Yarns and fabrics may also be advantageously pre-treated with a
10 fluorochemical prior to being coated or encapsulated by the silicone polymer resin in order to further increase the liquid, gel, spark, and molten metal shedding properties of the yarn or fabric. Exemplary fluorochemical compositions include, but are not limited to, MILEASE F-14N, F-34, F-31X and F-53 sold by ICI Americas, Inc.; PHOTOTEX FC104, FC461, FC731, FC208 AND FC232 sold by Ciba/Geigy;
15 TEFLON polymers such as TEFLON G, NPA, SKF, UP, UPH, PPR, N and MLV, sold by DuPont; ZEPEL polymers such as ZEPEL B, D, K, RN, RC, OR, HT, 6700 AND 7040, also from DuPont; SCOTCHGUARD sold by 3M.

 MILEASE F-14 contains approximately 18% perfluoroacrylate copolymer, 10% ethylene glycol, 7% acetone, and 65% water. MILEASE F-31X is a dispersion
20 of fluorinated resin, acetone and water. ZEPEL 6700 is comprised of 15-20% perfluoroalkyl acrylic copolymer, 1-2% alkoxylated carboxylic acid, 3-5% ethylene glycol, and water, and has a pH of 2-5. ZEPEL 7040 is similar to ZEPEL 6700 but further contains 7-8% acetone. SCOTCHGUARD is comprised of aqueously dispersed fluorochemicals in polymeric form.

25 Liquid repellant fluorochemical compositions are saturated into the fabric or yarn to completely and uniformly wet the fabric or yarn. This may be performed by dipping the fabric or yarn in a bath of liquid composition or padding the composition onto and into the fabric or yarn. After applying the fluorochemical composition to the fabric or yarn, the water (or other liquid carrier) and other volatile components of the
30 composition are removed by conventional techniques to provide a treated fabric or yarn that is impregnated with the dried fluorochemical. In one embodiment, the saturated fabric or yarn is compressed to remove excess composition. It is then

heated to remove the carrier liquid by evaporation (*e.g.*, at a temperature of about 130-160°C for a period of time about 2-5 minutes). If the fluorochemical is curable, heating may also catalyze or trigger curing.

The fluorochemical may also contain a bonding agent in order to strengthen the bond between the fluorochemical and the yarn or fabric to which it is applied. Exemplary bonding agents include Mobay SILOPREN bonding agent type LSR Z 3042 and NORSIL 815 primer.

When included, the fluorchemical is preferably applied in an amount in a range of about 1% to about 10% by weight of the original yarn or fabric, more preferably in an amount in a range of about 2% to about 4% by weight of the original yarn or fabric.

III. EXAMPLES

Examples 1-62 illustrate various embodiments of protective fabrics that have unexpectedly been found to protect a wearer against the effects of hot heat capacity materials, such as hot molten metals, hot oily liquids, hot gels, hot solids, and hot sparks and also hot corrosive materials, such as hot acids. Examples 1-61 provide examples of useful proactive fabrics and Example 62 describes comparative testing of a 70:30 O-Pan and p-aramid coated or encapsulated fabric as compared to an uncoated 70:30 wt% blend of O-Pan and p-aramid.

Example 1

A protective fabric made from a yarn having a 70:30 wt% blend of O-Pan and p-aramid, respectively, is encapsulated with a liquid shedding and strengthening silicone-based polymer as follows. First, the fabric is placed under tension. Second, the tensioned fabric is drawn through a vessel containing a silicone-based polymer resin. Third, the silicone-based polymer resin is subjected to localized shear-thinning forces produced by a rapidly spinning shearing blade adjacent to a surface of the fabric in order for the shear-thinned resin to encapsulate the yarn of the fabric and at least partially penetrate into interstitial spaces of the yarn. The viscosity of the silicone-based polymer resin is sufficiently low that it does not plug the spaces between the individual yarn strands of the fabric. Fourth, the treated tensioned fabric is removed from the vessel containing the silicone-based polymer resin. Fifth, the

treated fabric is heated in order to cure the silicone-based polymer resin and form the strengthening and liquid-shedding coating over the yarn.

The resulting protective fabric not only provides has liquid-shedding properties, but it unexpected provides a wearer against the effects of hot high heat capacity materials, such as hot molten metals, hot oily liquids, hot gels, hot solids, and hot sparks, and also hot corrosive materials, such as hot hydrochloric acid and other acids.

Example 2

A protective fabric made from a yarn having a 60:20:20 wt% blend of O-Pan, p-aramid, and m-aramid, respectively, is treated in the manner discussed in Example 1. The resulting fabric is somewhat stronger and more durable than the fabric obtained in Example 1 as a result of including a blend of strengthening fibers.

Example 3

A protective fabric made from a yarn consisting of 100% O-Pan is treated in the manner discussed in Example 1. Even though the fabric made from 100% O-Pan is relatively weak and fragile, treatment with the silicone polymer greatly increases the tensile strength, abrasion resistance, and durability so as to be acceptable for applications for which the fabric would otherwise be unacceptable absent the encapsulation treatment.

Example 4

A protective fabric made from a yarn having a 40:20:20:20 wt% blend of O-Pan, p-aramid, fire retardant wool, and PBI, respectively, is treated in the manner discussed in Example 1.

Example 5

A protective fabric made from a yarn having a 60:40 wt% blend of O-Pan and m-aramid, respectively, is treated in the manner discussed in Example 1. This fabric is significantly stronger to begin with compared to the fabrics of Example 1 as a result of include more strengthening fibers, but is less fire retardant and heat resistant.

Example 6

A protective fabric made from a yarn having a 90:10 wt% blend of O-Pan and PBI, respectively, is treated in the manner discussed in Example 1. This fabric is not as strong as compared to the fabrics of Examples 1, 2, 4 and 5 as a result of including

less strengthening fibers, but is more fire retardant and heat resistant as a result of including 10% PBI.

Example 7

5 A protective fabric made from a yarn having a 60:10:15:15 wt% blend of O-Pan, p-aramid, polyvinyl chloride, and m-aramid, respectively, is treated in the manner discussed in Example 1. This fabric is quite strong as compared to previous examples as a result of including more and more types of strengthening fibers, but is less fire retardant and heat resistant.

Examples 8-14

10 The protective fabrics of Examples 1-7 are pretreated with a fluorochemical prior to encapsulation with the silicone polymer. The fluorochemical is saturated into the fabric as a solution or suspension with a solvent. Excess fluorochemical composition is removed from the saturated fabric by applying pressure. Thereafter, the fluorochemical composition is heated in order to remove the solvent by evaporation
15 and dry the fluorochemical. After applying the silicone polymer according to Example 1, the fluorochemical remains at least partially impregnated within the protective fabric.

The fluorochemical further enhances the liquid-shedding properties of the protective fabric beyond what is provided by the silicone polymer encapsulation of
20 Examples 1-7.

Examples 15-33

Various protective fabrics are manufactured using any of the fabrics utilized in Examples 1-7. The silicone polymer coating used to treat the fire retardant and heat resistant fabric(s) according to Examples 15-33 are set forth in Table I below. The
25 amount of silicone resin in the polymer coating is in all cases 100 parts. The "mixture ratio" refers to the ratio of packaged components as supplied by the manufacturer.

Table I

Example	Silicone Resin	Mixture Ratio	Substituted Benzophenone	Parts	Other Additives	Part
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15	Silopren® LSR 2530	1:1	Uvinul 400	5	7127 Accelerator ¹	5/10
16	Silastic® 595 LSR	1:1	Uvinul 400	5	Syl-off® 7611 ²	50
17	SLE 5100, Liquid BC- 10	10:1 1:1	Uvinul 400	5	Sylox® 2 ³	8
18	Silopren® LSR 2530	1:1	Uvinul 400	5	Hydral® 710 ⁴	10
19	Silopren® LSR 1530	1:1	Uvinul 400	5	Silopren® LSR Z3042 ⁵	1
20	SLE 5500	10:1	Uvinul 400	5		
21	Silopren® 2430	1:1	Uvinul 400	5		
22	SLE 5300	10:1	Uvinul 400	5		
23	SLE 5106	10:1	Uvinul 400	5		
24	Silopren® LSR 2530	1:1	Uvinul 400	5	Flattening Agent OK412® ⁶	4
25	Silopren® LSR 2530	1:1	Uvinul 400	5	Nalco® 1SJ-612 Colloidal Silica ⁷	50
26	Silopren® LSR 2530	1:1	Uvinul 400	5	Nalco® 1SJ-612 Colloidal Alumina ⁸	50
27	Silastic® 595 LSR	1:1	Uvinul 400	5	200 Fluid ⁹	7
28	Silopren® LSR 2530	1:1	Uvinul 400	5		
29	Silastic® 595 LSR	1:1	Uvinul 400	5	Zepel® 7040 ¹⁰	3
30	Silastic® 595 LSR	1:1	Uvinul 400	5	Zonyl® UR ¹¹	1/10

31	Silastic® 595 LSR	1:1	Uvinul 400	5	Zonyl® FSN-100 ¹²	1/10
32	Silopren® LSR 2530	1:1	Uvinul 400	5	DLX- 600® ¹³	5
33	Silopren® LSR 2530	1:1	Uvinul 400	5	TE-3608® ¹⁴	5

¹ 7127 Accelerator (Dow Corning) is a polysiloxane

² Syl-off® (Dow Corning) is a cross-linker

³ Sylox® 2 (W.R. Grace & Co.) is a synthetic amorphous silica

⁴ Hydral® 710 (Alcoa) is a hydrated aluminum oxide

5 ⁵ Silopren® LSR Z3042 (Mobay) is a silicone primer (bonding agent) mixture

⁶ Flattening Agent OK412® (Degussa Corp.) is a wax coated silicon dioxide

⁷ Nalco® 1SJ-612 Colloidal Silica (Nalco Chemical Co.) is an aqueous solution of silica and alumina

⁸ Nalco® 1SJ-612 Colloidal Alumina (Nalco Chemical Co.) is an aqueous colloidal alumina dispersion

⁹ 200 Fluid (Dow Corning) is a 100 cps viscosity dimethylpolysiloxane

10 ¹⁰ Zepel® 7040 (DuPont) is a nonionic fluoropolymer

¹¹ Zonyl® UR (DuPont) is an anionic fluorosurfactant

¹² Zonyl® FSN-100 (DuPont) is a nonionic fluorosurfactant

¹³ DLX-600® (DuPont) is a polytetrafluoroethylene micropowder

¹⁴ TE-3608® (DuPont) is a polytetrafluoroethylene micropowder

15

The silicone polymer resin and other components are mixed using a Hockmayer F dispersion blade at low torque and high shear. The protective fabric is tensioned and passed through a bath containing the silicone resin composition. Localized high shear is applied to the silicone resin composition near the surface of the fabric in order to coat the yarn strands comprising the fabric at a rate of 1.0 oz/sq. yd. The fabric is passed through the polymer resin composition several times to ensure thorough impregnation. After impregnation, the impregnated fabric is removed from the silicone polymer composition bath and passed through a line oven of approximately 10 yards in length, at 4-6 yards per minute, and cured at a temperature of 325-350°F.

25

Examples 34-60

Various protective fabrics are manufactured according to any of Examples 8-14. The fluorochemical compositions used to pretreat the fire retardant and heat resistant fabric(s) according to Examples 34-60 prior to application of the silicone resin composition (which may comprise any of the compositions of Examples 15-33 in Table I) are set forth in Table II below.

Table II

Example	Flurochemical
34	Milease® F-14N
35	Milease® F-34
36	Milease® F-31X
37	Milease® F-53
38	Phobotex® FC104
39	Phobotex® FC461
40	Phobotex® FC731
41	Phobotex® FC208
42	Phobotex® FC232
43	Teflon® G
44	Teflon® NPA
45	Teflon® SKF
46	Teflon® UP
47	Teflon® UPH
48	Teflon® PPR
49	Teflon® N
50	Teflon® MLV
51	Zepel® B
52	Zepel® D
53	Zepel® K
54	Zepel® RN
55	Zepel® RC
56	Zepel® OR
57	Zepel® HT

58	Zepel® 6700
59	Zepel® 7040
60	Scotchguard®

Prior to applying the fluorochemical composition, the protective fabric is washed with detergent, rinsed thoroughly, and hung to air dry. Thereafter, the fabric is soaked in water and then wrung dry to retain 0.8 g water/g fabric. The fabric is then treated with a solution or suspension (*e.g.*, a 2% solution) of the fluorochemical composition, taking into account the water already soaked into the fabric (*e.g.*, using a 2.5% solution of the fluorochemical). The pretreated fabric is wrung through a wringer and air dried. The fabric is then heated in an oven for 1 minute at 350°F to remove any remaining solvent and sinter the fluorochemical. The fluorochemical treated fabric is then coated with a silicone polymer composition (*e.g.*, a composition from one of Example 15-33).

Example 61

Various protective fabrics are manufactured using the fabrics disclosed in Examples 1-7, the silicone resin compositions of Examples 15-33, and the fluorochemical compositions of Examples 34-60 (*i.e.*, a wide range of different liquid, gel, spark, and molten metal-shedding and strengthened fire retardant and heat resistant fabrics are manufactured using every possible combination of fabrics, silicone resin compositions, and fluorochemical compositions of Examples 1-7, 15-33 and 34-60, respectively).

The protective fabrics can be used in the manufacture of a wide variety of clothing and other articles where protection against contact with hot high heat capacity materials and/or hot corrosive materials is desirable. Examples include, but are not limited to, clothing, jump suits, gloves, socks, welding bibs, welding sleeves, welding mask shrouds (*e.g.*, to protect the neck), breacher's coats (*e.g.*, as worn by military or other personnel while cutting through metal), fire blankets, padding, protective head gear, linings, undergarments, bedding, drapes, and the like.

Example 62

A fire retardant and heat resistant fabric (referred to hereafter as C59) comprising a 86:14 wt% blend of O-Pan and p-aramid without a silicone-based

polymer coating was tested as compared to the same fabric (referred to hereafter as C59E) with a silicone-based polymer coating. The testing was in accordance with ASTM standard F955-03 entitled "Evaluating Heat Transfer through Materials for Protective Clothing upon Contact with Molten Substances." The standardized conditions for molten iron impact evaluations include pouring 1 kg \pm 0.1 kg of molten iron at a minimum temperature of 2800°F onto fabric samples attached to a calorimeter board. The testing set up is shown in Figures 1-3. The calorimeter board 100 was oriented at an angle of 70° from the horizontal and molten metal 102 dropped from a height of 12 inches onto a fabric sample 104 placed over calorimeter board 100. The ladle 106 containing the molten metal was rotated against a rigid stop and the molten metal 102 dumped onto the test fabric 104. The orientation of the ladle 106, calorimeter board 100, and calorimeters 108 before dumping is illustrated in Figure 1.

Each fabric 104 to be tested was placed on the calorimeter board 100 and held in place with clips 110 along the upper edge of board 100. A preheated ladle 106 was filled with molten iron 102 from an induction furnace held at a temperature of approximately 2925°F. The molten metal weight was determined with an electronic balance and was maintained at 1 kg \pm 0.1 kg. The filled ladle 106 was transferred to the ladle holder and splashed onto the fabric (Figure 2). A fixed delay of 25 seconds after the start of the furnace pour was used to maintain a consistent metal impact temperature. Empirical testing has shown that metal temperature decreases by approximately 75-100°F after the 25 second delay. The molten metal 102 was poured from the ladle 106 onto the fabric 104 and the results assessed. Each fabric 104 was tested using an undergarment consisting of a single layer of all-cotton T-shirt.

Visual examination was conducted on the impact fabric 104 for each sample tested. The visual appearance of each fabric 104 was subjectively rated in four categories after impact with molten metal 102. These categories were (1) charring, (2) shrinkage, (3) metal adherence, and (4) perforation. The rating system is outlined below, and the results are presented in Table III, below.

The char rating describes the extent of scorching, charring, or burning sustained by the fabric. The shrinkage rating provides an indication of the extent of the fabric wrinkling caused by shrinkage occurring around the area of metal impact.

It is desirable to have a minimum amount of charring, wrinkling, and shrinkage during or after an impact event. Metal adherence refers to the amount of metal sticking to the fabric. The perforation rating describes the extent of fabric destruction in terms of the size, number of holes created, and penetration of molten metal through the fabric. It is desirable to have no perforation or penetration of molten metal through the fabric. The rating system uses numbers one through five in each category, with "1" representing the best behavior and "5" representing worst behavior.

Grading System Used to Evaluate Fabric Damage

The fabric samples were evaluated visually for charring, shrinkage, and perforation, to provide an indication of the extent of damage to the outer impacted layer. Five grades were used in evaluating the extent of charring:

- 1 = slight scorching, fabric had small brown areas
- 2 = slight charring, fabric was mostly brown in impacted area
- 3 = moderate charring, fabric was mostly black in impacted area
- 4 = charred, fabric was black and brittle, cracked when bent
- 5 = severely charred, large holes or cracks, very brittle

Shrinkage was evaluated by laying the fabric on a flat surface and observing the extent of fabric wrinkling around the splash area. Shrinkage was evaluated using five categories:

- 1 = no shrinkage
- 2 = slight shrinkage
- 3 = moderate shrinkage
- 4 = significant shrinkage
- 5 = extensive shrinkage

The adherence rating refers to the amount of metal sticking to the front of the fabric. Adherence of metal was rated using five categories:

- 1 = none
- 2 = small amount of metal adhered to face or back of fabric
- 3 = a moderate amount of metal adhered to the fabric
- 4 = substantial adherence of the metal to the fabric
- 5 = large amount of adherence of metal to the fabric

Perforation was evaluated by observing the extent of destruction of the fabric, usually by holding it up to a light. Five grades were used in evaluating perforation:

1 = none

2 = slight, small holes impacted area

5 3 = moderate, holes in fabric

4 = metal penetration through the fabric, some metal retained on the fabric

5 = heavy perforation, the fabric exhibited gaping holes or large cracks or substantial metal penetration to the back side

The results are presented in Table III, below:

10

Table III

Material Designation	Charring	Shrinkage	Adherence	Perforation
C59 Run 1	4	2	2	2
C59 Run 2	4	2	2	2
C59E Run 1	3	1	1	1
C59E Run 2	3	1	1	1
C59E Run 3	3	1	1	3

The calorimeter board 100 to which the fabrics 104 were attached was constructed according to ASTM standard F955-03. The board 100 contained two 4 cm diameter, 1/16 inch thick copper disks 108. One copper disk was located at the point of molten metal impact, and the second was located 4 inches below the first. Each copper disk calorimeter 108 contained a single 30-gauge iron/constantan Type J thermocouple inserted into the back of the calorimeter 108. The thermocouple output from the calorimeter 108 was recorded with a high precision digital data acquisition system. The temperature rise for both calorimeters 108 was plotted for 45 seconds for each fabric sample tested. The total heat energy that flowed through the fabric was calculated at each time step using the following formula:

$$Q = \frac{m \times C_p \times (Temp_{final} - Temp_{initial})}{Area}$$

where:

Q = heat energy (J/cm^2),

m = mass of copper slug (g),

C_p = average heat capacity of copper during the temperature rise
($\text{J}/\text{g}^\circ\text{C}$),

$\text{Temp}_{\text{final}}$ = final temperature of calorimeter at $\text{time}_{\text{final}}$ ($^\circ\text{C}$),

$\text{Temp}_{\text{initial}}$ = initial temperature of calorimeter at $\text{time}_{\text{initial}}$ ($^\circ\text{C}$),

Area = area of copper calorimeter.

This heat energy curve was compared to an empirical human predicted
second-degree skin burn injury model (Stoll Curve). The Stoll Curve was calculated
from the following formula:

$$\text{Stoll Curve } (\text{J}/\text{cm}^2) = 5.0204(t_j^{0.2901})$$

where t_j is the time after molten metal impact.

Figure 4A shows temperature rise at each thermocouple through the C59
fabric not including a silicone-based polymer coating. Figure 4B shows the heat
transfer through the C59 fabric not including the silicone-based polymer coating, as
well as the theoretical Stoll Curve. Figure 5A shows temperature rise at each
thermocouple through the C59E fabric including a silicone-based polymer coating.
Figure 5B shows the heat transfer through the C59E fabric including the silicone-
based polymer coating, as well as the theoretical Stoll Curve. These results are
summarized in Table IV below.

Table IV

Material Designation	Max. ΔT @ Top Calorimeter	Max. ΔT @ Bottom Calorimeter	Time to 2 nd degree burn
C59 Run 1	25.2 $^\circ\text{C}$	16.7 $^\circ\text{C}$	2.2 seconds
C59 Run 2	19.3 $^\circ\text{C}$	17.7 $^\circ\text{C}$	4.8 seconds
C59E Run 1	10.3 $^\circ\text{C}$	10.9 $^\circ\text{C}$	None
C59E Run 2	10.1 $^\circ\text{C}$	10.5 $^\circ\text{C}$	None
C59E Run 3	8.3 $^\circ\text{C}$	12.8 $^\circ\text{C}$	None

As seen, the C59 fabrics alone are only able to slow the occurrence of a second degree burn, which would occur after 2.2 seconds and 4.8 seconds, respectively, according to the tests run. The C59E fabrics which include the silicone coating, on the other hand, will actually prevent the formation of a second degree burn to the wearer. This is a result of the synergistic combination of the C59 fabric and the silicone polymer coating. In short, the C59 fabric alone is not able to prevent the formation of a second degree burn. Similarly, the use of another fabric (*e.g.*, cotton and/or nylon) encapsulated with silicone (as discussed in, *e.g.*, U.S. Patent Nos. 4,666,765, 5,004,643, 5,209,965, 5,418,051, 5,856,245, 5,869,172, 5,935,637, 6,040,251, 6,071,602, 6,083,602, 6,129,978, 6,289,841, 6,312,523, 6,342,280 and 6,416,613) would likewise not be able to prevent a second degree burn, as the molten iron would heat the inner core cotton or nylon material, at which point it would decompose or burn, and the fabric would be readily perforated.

The surprising and particularly advantageous result of second degree burn prevention illustrated by the comparative example is possible because of the synergistic effects of the C59 O-Pan based fabric combined with the silicone-based polymer coating applied over the fabric. The silicone-based coating provides the coated fabric with an improved ability to shed the molten metal quickly, rather than allowing it to remain on the coated fabric surface, while the C59 O-Pan based fabric has sufficient fire retardance and heat resistance to maintain fabric integrity and minimize heat conduction to the underlying user's skin.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed is:

CLAIMS

1. A method of protecting an object from a hot high capacity material or hot corrosive material, comprising:
covering an object with a protective fabric comprised of:
 - 5 yarn strands composed of one or more types of fire retardant and heat resistant polymer fibers and/or filaments having an LOI of at least about 50 and that do not burn when exposed to heat or flame having a temperature of about 3000° F; and
 - an outer layer coating at least a portion of the fabric or yarn strands, the outer layer comprising a liquid-shedding and strengthening polymer coating; and
 - 10 exposing the object to a hot high capacity material and/or hot corrosive material having a temperature of at least about 300 °F (150 °C).
2. A method as in claim 1, wherein the object is a human or animal.
- 15 3. A method as in claim 1, wherein the hot high capacity material or hot corrosive material comprises a hot molten metal.
4. A method as in claim 1, wherein the hot high capacity material or hot corrosive material comprises heating oil.
5. A method as in claim 1, wherein the hot high capacity material or hot
20 corrosive material comprises a gel.
6. A method as in claim 1, wherein the hot high capacity material or hot corrosive material comprises burning phosphorus.
7. A method as in claim 1, wherein the hot high capacity material or hot corrosive material comprises a solid.
- 25 8. A method as in claim 1, wherein the hot high capacity material or hot corrosive material comprises an acid.
9. A method as in claim 1, wherein the hot high capacity material or hot corrosive material has a temperature of at least about 400 °F (200 °C).
10. A method as in claim 1, wherein the hot high capacity material or hot
30 corrosive material has a temperature of at least about 500 °F (260 °C).
11. A method as in claim 1, wherein the hot high capacity material or hot corrosive material has a temperature of at least about 600 °F (315 °C).

12. A method as in claim 1, wherein the hot high capacity material or hot corrosive material has a temperature of at least about 750 °F (400 °C).

13. A method as in claim 1, wherein the hot high capacity material or hot corrosive material has a temperature of at least about 950 °F (510 °C).

5 14. A method as in claim 1, wherein the hot high capacity material or hot corrosive material has a temperature of at least about 1150 °F (620 °C).

15. A method as in claim 1, wherein the fire retardant and heat resistant polymer fibers and/or filaments comprise oxidized polyacrylonitrile.

10 16. A method as in claim 15, wherein the oxidized polyacrylonitrile is included in an amount in a range of about 25% to about 99.9% by weight of the yarn, the yarn further comprising one or more types of strengthening fibers and/or filaments.

15 17. A method as in claim 16, wherein the strengthening fibers and/or filaments comprise at least one of p-aramid, m-aramid, polybenzimidazole, polybenzoxazole, polyphenylene-2,6-benzobisoxazole, modacrylic, polyvinyl halide, wool, fire resistant polyester, nylon, rayon, cotton, or melamine.

20 18. A method as in claim 1, wherein the fabric or yarn strands further comprise at least one strengthening filament selected from steel, stainless steel, steel alloy, titanium, titanium alloy, aluminum, aluminum alloy, copper, copper alloy, and high strength ceramics that includes at least one oxide of Al, Zr, Ti, Si, Fe, Co, Ca, Nb, Pb, Mg, Sr, Cu, Bi, or Mn.

19. A method as in claim 1, wherein the liquid-shedding and strengthening polymer coating comprises at least one type of cured silicone polymer resin.

25 20. A method as in claim 1, further comprising at least one fluorochemical at least partially impregnated within the fabric or yarn strands that further imparts liquid-shedding capability to the protective article.

21. A method as in claim 1, wherein the outer layer comprises an outer shell that encapsulates the yarn strands.

30 22. A method of protecting a person from a hot high capacity material, comprising:

covering at least a portion of a person with a protective fabric comprised of:

yarn strands composed of oxidized polyacrylonitrile; and
an outer layer coating at least a portion of the fabric or yarn
strands, the outer layer comprising a liquid-shedding and strengthening
polymer coating; and

5 exposing the object to a hot high capacity material selected from hot
molten metal, hot oily liquid, hot gel, hot solid, and hot sparks and having a
temperature of at least about 300 °F (150 °C).

23. A method of protecting a person from hot acid, comprising:

covering at least a portion of a person with a protective fabric
10 comprised of:

yarn strands composed of oxidized polyacrylonitrile; and
an outer layer coating at least a portion of the fabric or yarn
strands, the outer layer comprising a liquid-shedding and strengthening
polymer coating; and

15 exposing the object to hot acid having a temperature of at least about
300 °F (150 °C).

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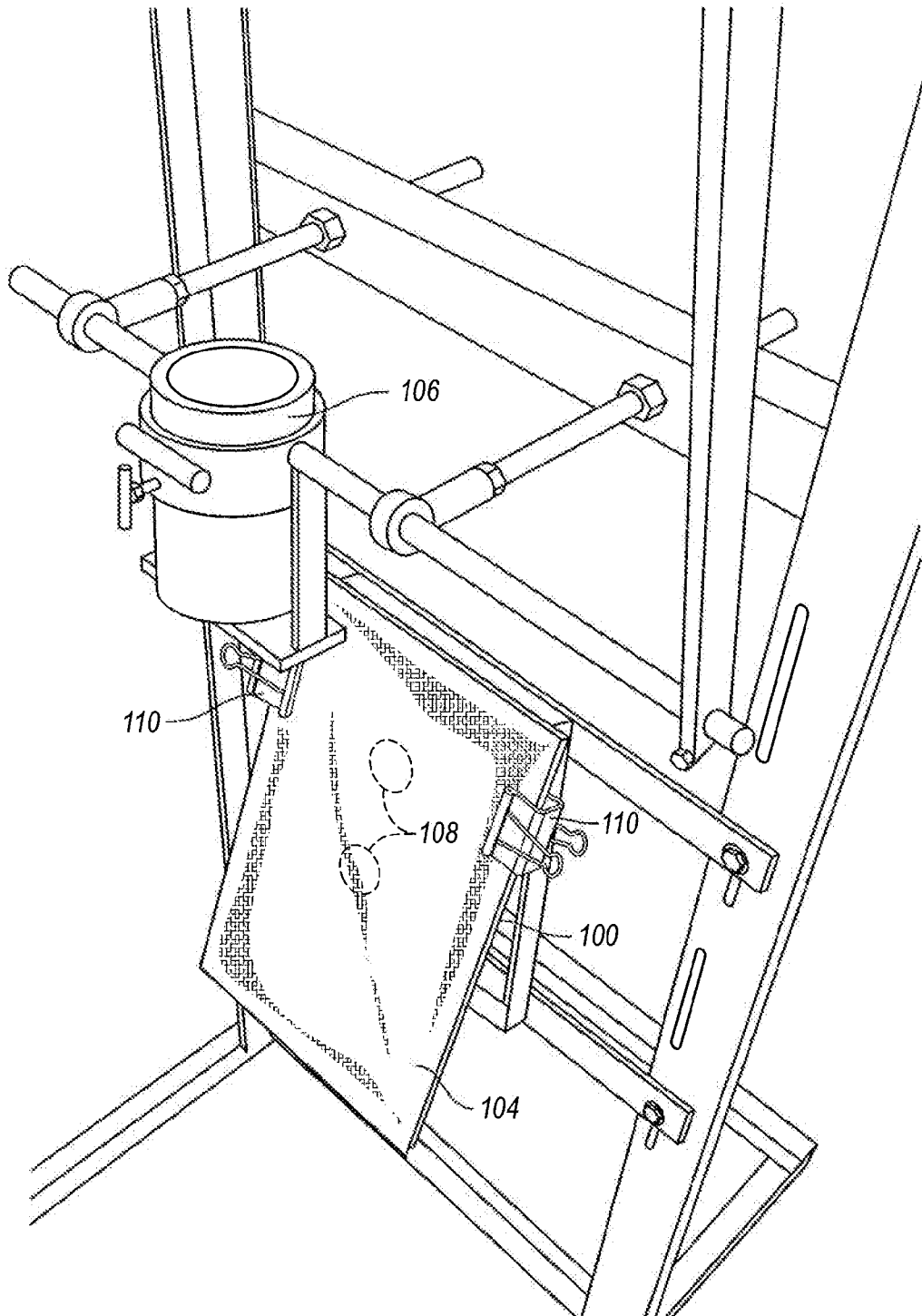


Fig.1

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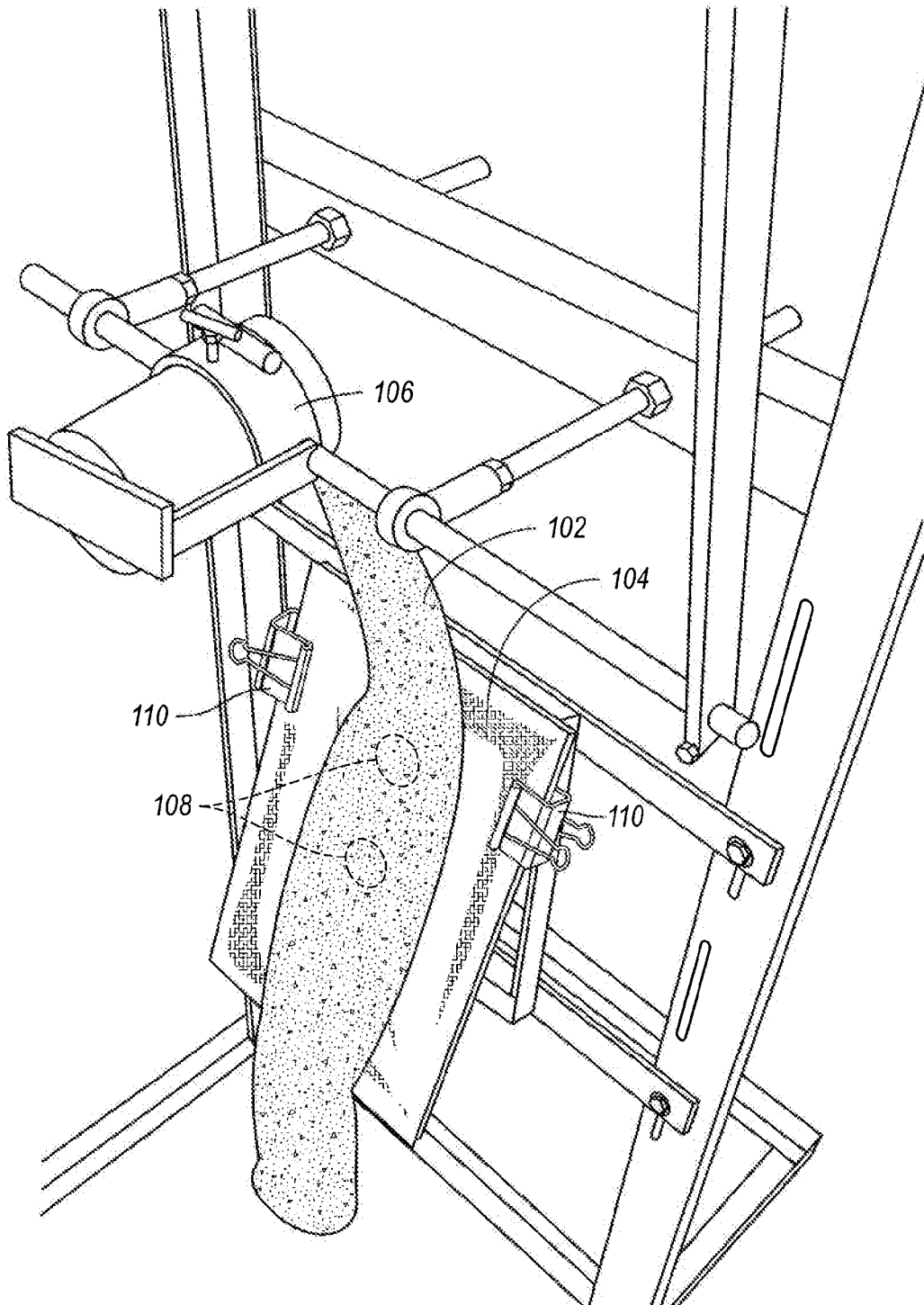
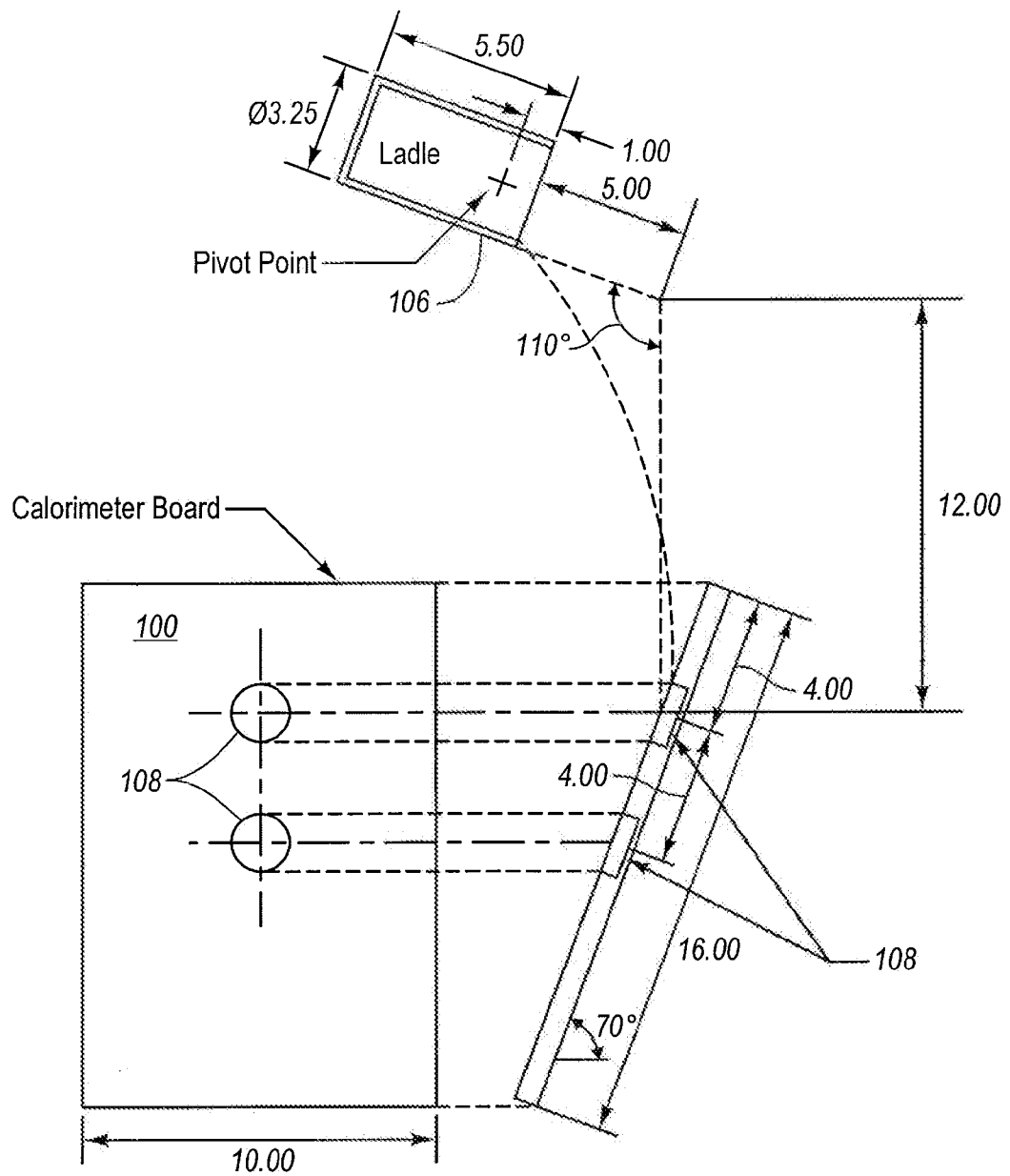
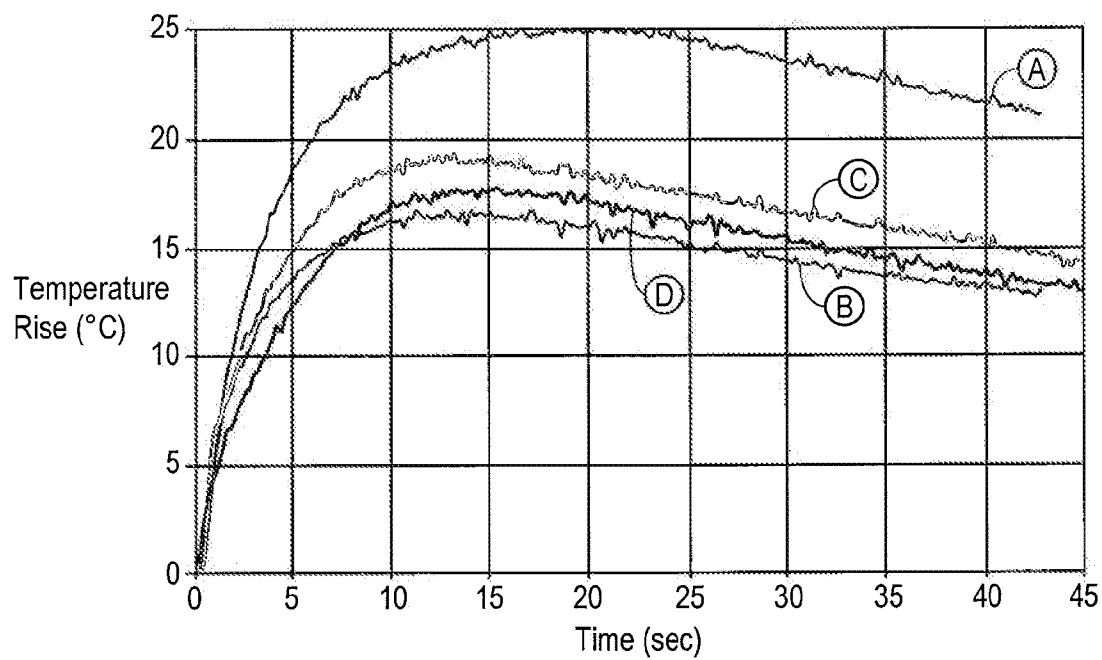


Fig.2

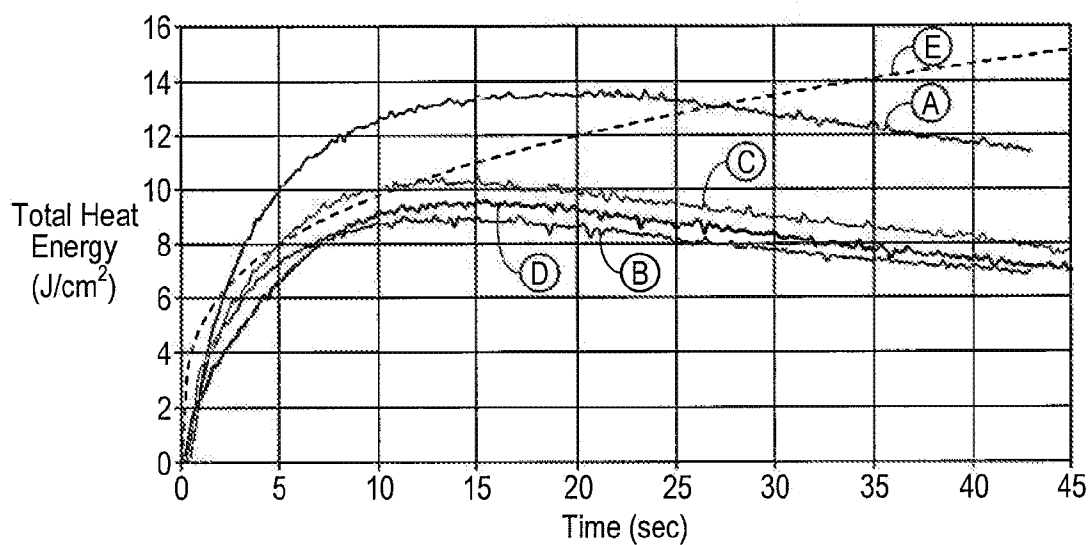
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**Fig. 3**

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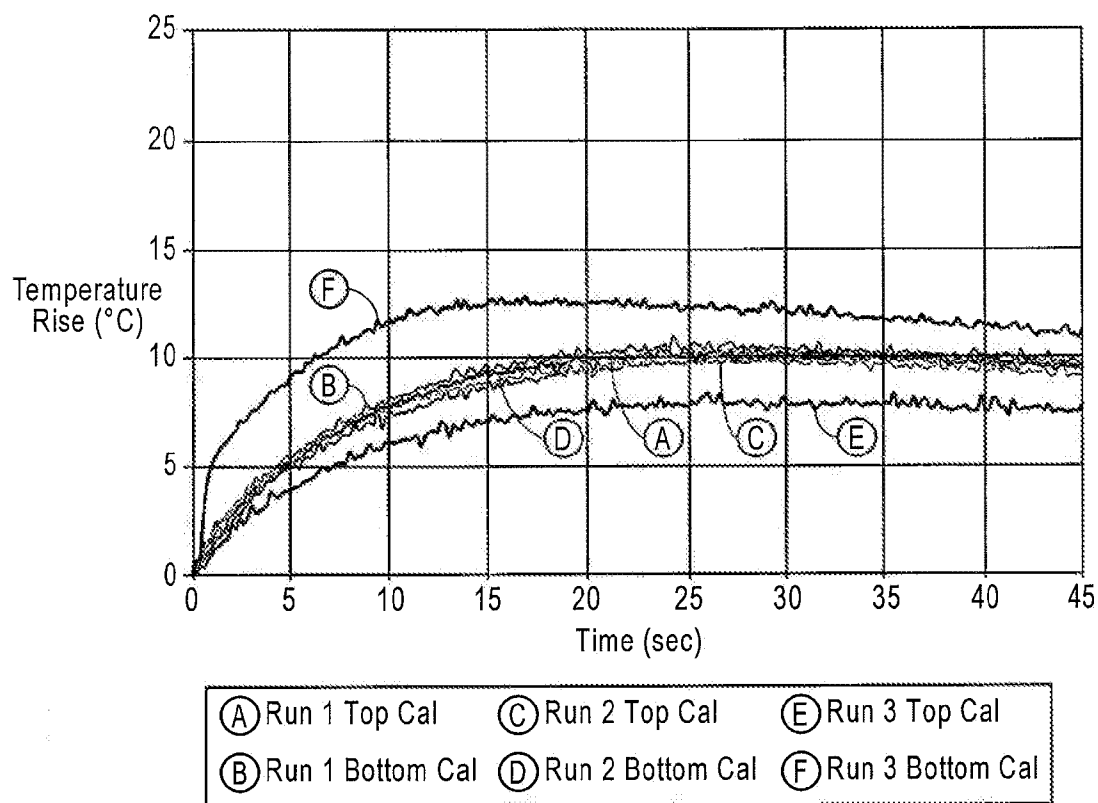
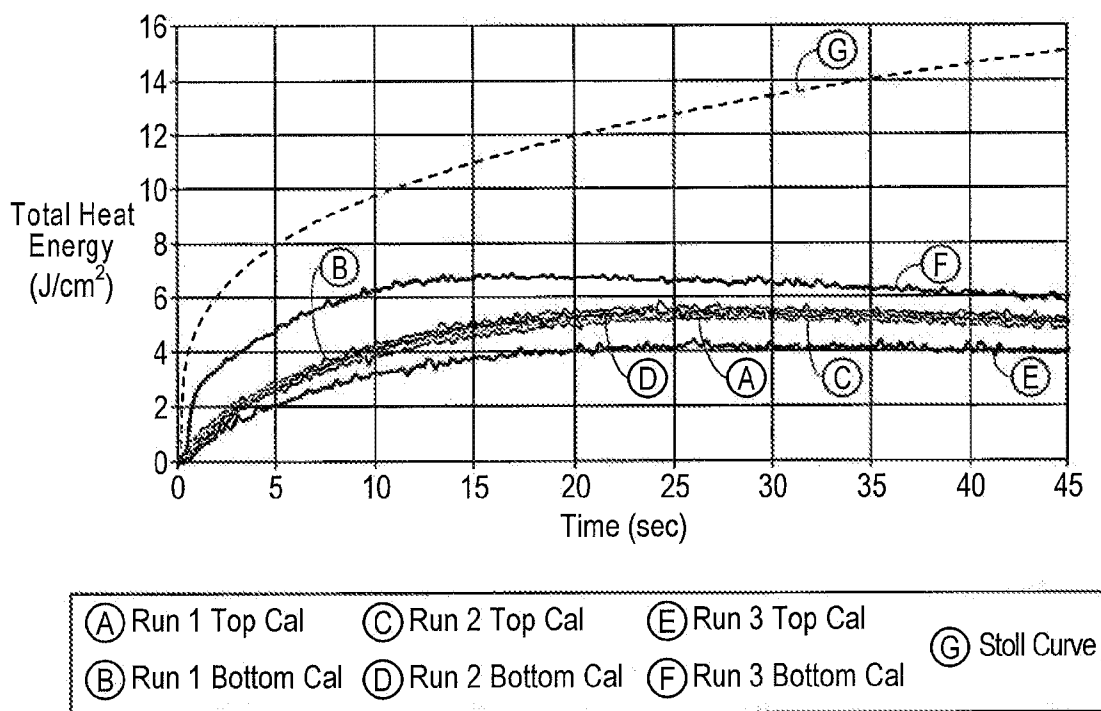
(A) Run 1 Top Cal (B) Run 1 Bottom Cal (C) Run 2 Top Cal (D) Run 2 Bottom Cal

Fig. 4A

(A) Run 1 Top Cal (B) Run 1 Bottom Cal (C) Run 2 Top Cal (D) Run 2 Bottom Cal (E) Stoll curve

Fig. 4B

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**Fig. 5A****Fig. 5B**