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(54) Title: FLAME RESISTANT BALLISTIC COMPOSITE
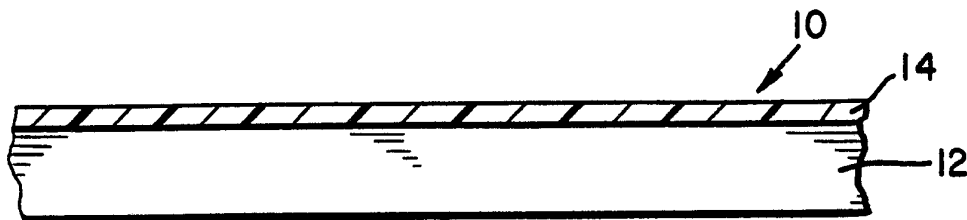
(57) Abstract

This invention relates to a fire retardant compound comprising at least one fibrous layer comprising a network of fibers (12) such as high strength polyethylene or aramid fibers in a matrix such as a blend of a vinyl ester and a polyurethane, and a fire retardant layer (14) comprised of a particulate fire retardant material which decompose and heating to a gaseous material such as magnesium hydroxide dispersed in a matrix comprised of a relatively high char yield resin such as a cured phenolic cyanate resin.

FLAME RESISTANT BALLISTIC COMPOSITE

Background of the Invention

1. Field of the Invention

This invention relates to flame resistant
articles. More particularly, this invention relates
to ballistic or impact resistant articles having
improved flame resistance.

2. Prior Art

Ballistic articles such as bulletproof vests,
helments, structural members of helicopters and other
military equipment, vehicle panels, briefcases,
raincoats and umbrellas containing hihgh strength
fibers are known. Fibers conventionally used include
aramide fibers such as poly(phenylenediamine
terephthalamide), graphite fibers, nylon fibers,
ceramic fibers, glass fibers and the like. For many
applications, such as vests or parts of vests, the
fibers are used in a woven or knitted fabirc. For
many of the applications, the fibers anre encapsulted
or embedded in a matrix material.

In "The Application of High Modulus Fibers to
Ballistic Protection", R.C. Laible et al., J.
Macromol. Sci.-Chem., A7(1), pp. 295-322, 1973, it is
indicated on p. 298 that a fourth requirement is that
the textile material have a high degree of heat
resistance. In an NTIS publication, AD-A018 958 "New
Materials in Construction for Improved Helmets", A.L.
Alesi et al., a multilayer highly oriented
polypropylene film material (without matrix),
referred to as "XP", was evaluated against an aramid
fiber (with a phenolic/polyvinyl butyral resin
matrix. The aramid system was judged to have the
most promising combination of superior performance

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and a minimum of problems for combat helmet development.

USP 4,403,012 and USP 4,457,985 disclose ballistic resistant composite articles comprised of networks of high molecular wight polyethylene or polypropylene fibers, and matrices composed of olefin polymers and copolymers, unsaturated polyester resins, epoxy resings, and other resins curable below the melting point of the fiber.

A.L. Lastnik, et al., "The Effect of Resin Concentration and Laminating Pressures of KEVLAR Fabric Bonded with Modified Phenolic Resin", Tech. Report NATICK/TR--84/030, June 8, 1984; disclose that an interestitial resin, which encapsulates and bonds the fibers of a fabric, reduces the ballistic resistance of the result composite article.

US Patent Nos. 4,623,574 and 4,748,064 disclose a simple composite structure comprising high strength fibers embedded in an elasomeric matrix. The simple composite structure exhibits outstanding ballistic protection as compared to simple composites utilizng rigid matrices, the result of which are disclosed in the patent. Particularly effective are simple composites utilizing rigid matrices, the result of which are disclosed in the patents. Particularly effective are simple composites employing ultra-high molecular weight polyethylene and polypropylene such as disclosed in US Patent No. 4,413,110.

US Patent Nos, 4,737,402 and 4,613,535 disclose complex rigid composite articles having improved impact resistance which comprise a network of high strength fibers such as the ultra-high molecular weight polyethylene and polypropylene disclosed in US Patent No. 4,413,110 embedded in an elasomeric material and at least one additional rigid layer on a major surfact of the fibers in the matrix. It is disclosed that the composites have improved

resistance to environmental hazards, improved impact resistance and are unexpectedly effective as ballistic resistant articles such as armor.

US Patent 4,650,710 discloses a ballistic resistant fabric article which comprises at least one network of fibers selected from the group consisting of extended chain polyethylene, polypropylene, polyvinyl alcohol and polyacrylonitrile fibers coated with a low modulus elastomeric material.

US Patent 4,681,792 discloses a flexible article of manufacture comprising a plurality of first flexible layers arranged in a first portion of the article, each of said first layers consisting essentially of fibers having a tensile modulus of at least about 300 g/denier and a tenacity of at least about 15 g.denier and a plurality of second flexible layers arranged in a second portion of said article, each of said second flexible layers comprising fibers, the resistance to displacement of fibers in each of said second flexible layers being greater than the resistance to displacement in each of said first flexible layers.

US Patent 4,543,286 discloses a ballistic-resistant fabric article of manufacture comprising at least one network of extended chain polyolefin fibers selected from the group consisting of extended chain polyethylene and extended chain polypropylene fibers in a matrix, the fibers are coated with at least 0.01 to 200% of a polymer having ethylene or propylene crystallinity.

US Patent No. 4,916,000 discloses a composite of at least one layer which comprises a network of filaments in a matrix, wherein that ratio of thickness of the layer to filament diameteR is less than about 12.8.

US Patent No. 4,737,401 discloses composites of polyethylene, polyperopylene, polyvinyl alcohol and

polyacrylonitrile of low denier (under 500) and low
tensile modulus-(200 grams/denier).

   U.S. Patent No. 4,868,040 discloses the use of
5 Al(OH)₃ as a flame retardant in vinyl ester resin
matrixes to reduce smoke production and to enhance
flame retardancy of the armor composite.

   Fire retardant compositions are known. For
example, A.H. Landrocki, "Handbood of Plastic
10 Flammabiltiy Fuel and combustion Toxicology," (Noyes
Publication, 1983) disclosures the basic front line
of fire/flame retardants. Basically, flame
retardants for plastics function under heat to yield
products that would be more difficult to ignite than
15 the virgin plastics, or that do not propagate flame
as readily. They function in one or more ways. For
example, they absorb heat, thereby making sustained
burning more difficult, and they form nonflammable
char or coating that insulates the substrate from the
20 heat, excludes oxygen, and slows the rate of
diffusion of volatile, flammable pyrolysis fragments
from the substrate. Flame retardants for plastics
may also function by enhancing the decompositon of
the substrate, thereby accelerating its melting at
25 lower temperatures so that it drips or flows away
from the flame front and by evolving products that
stop or slow flame propagation. Still other flame
retardants for plastics may function by forming free
radicals that convert a polymer to less combustible
30 products and by excluding oxygen from possible
burning sites by coating resin particles.

   Fire-retardant chemicals available commercially
for plastics can be divided into two general classes,
unreactive additives and reactive monomers or
35 crosslinking agents. The unreactive additives are
generally added to the polymer during processing, but
do not react chemically with the other constituents
of the composition. The reactive types, on the other

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hand, chemically react with the polymer structure at some processing stage.

The ideal fire retardant additives should be inexpensive , colorless, easily incorporated into the polymer composition, compatible, stable to heat and light, efficient in its fire-retardant properties, nonmigrating, and have no adverse effects on the physical properties of the polymer. The toxicology of the additive is also of concern. Unfortunately, most presently available additives seldom meet all these requirements.

Additive flame-retardant systems are generally composed of both organic and inorganic materials acting to provide an optimum balance of flame retardance, physical properties and cost. Additive retardants are generally incorporated by compounding and are useful in a variety of polymer systems. These materials are generally used for thermoplastic resins, although there are exceptions. With few exceptions, additive resins are used to fire retard flexible polyurethane foams. Halogenated organic compounds, such as PVC, or decabromodiphenyl oxide (DBDPO) in combination with antimony oxide typifies this type of system. DBDPO has long been the standard of comparison in many rigid plastics. Other compounds of this type include polychlororene, chlorinated polyethylene, and chlorosulfonated polyethylene, chlorinated parraffins, tris(dichloropropyl)phosphate, methyl pentachlorostearate, and various chlorinated phosphates for polyurethane foams and topical fabric treatment; cycloaliphatic chlorine-containing flame retardants (with higher thermal stability) for thermoplastics like polypropylene and nylon; and chlorendic anhydride, which is used as an intermediate in making flame retardant polyesters and epoxy resins.

Reactive flame retardant systems contain
functional groups allowing them to be incorporated
directly into the polymer structure through chemical
reactions. The main advantage of this type of fire
retardant is the permanence of the fire retardancy
imparted. In most cases, chemically reacting the
fire retardant into the polymer essentially
eliminates long-term migration of the fire retardant.

Reactive flame retardants are primarily used in
unsaturated polyesters, epoxy resins and polyurethane
foams. Two of the most popular reactive flame
retardants are tetrabrombisphenol A and
dibromomononeopentyl and tetrabromophthalic glycol.
Other reactive flame retardants include chlorendic
acid and chlorendic anhydride, tetrabromophthalic and
tetrachlorophthalic anhydride, and diallyl
chlorendate. Other reactive flame retardants vary
significantly in functionality and can be useful in
many polymer reactions and applications. Reactive
polyols which contain halogen groups, phosphorus, or
both are used for flame-retardant urethane foam
applications. These materials can be used alone, or
with other flame retardants.

It is known that certain types of resins exhibit
fire retardant properties. For example,
thermosetting polymers differ from thermoplastics in
that they become chemically crosslinked during final
molding and curing. For most practical purposes,
they can no longer be melted, reshaped or dissolved.
Thermosetting resins are produced in large volume and
are extensively used in the construction, housing,
and large applicance industries where they may
contribute significantly to the fire load in any
particular area or product. For this reason, their
fire safety characteristics are important. Because
of their crosslinked nature, thermosets generally do
no soften or drip when exposed to a flame, as do many

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thermoplastic materials. Their flammability is a
function of the thermal stability of the primary
chemical bonds and the ease with which volatile

5   gaseous products can be produced by pyrolytic
processes to provide fuel for a self-sustaining
fire. Many thermosets (e.g. the phenolic resins)
provide very little flammable fuel when heated by an
ignition source. They produce an insulating char

10 that can only be oxidized at extremely high
temperatures and/or high oxygen concentrations.
Burning of such materials can be a slow process under
many conditions, since the polymer substrate is
protected by the surface char. Such resins are

15 inherently fire-retardant and will pass many common
laboratory tests without the need for a
fire-retardant modification or additive. Their fire
retardance is, however, a function of the mechancial
ability of the insulating char and is limited by the

20 resistance of elemental carbon to oxidation. Other
thermosets (e.g. styrenated polyester resins) do not
form chars and burn readily.

                    SUMMARY OF THE INVENTION

25
        The present invention provides an article of
manufacture comprising two or more layers, at least
one of said layers is a fibrous layer comprised of a
network of fibers composed of one or more polymeric

30 materials in a matrix material, and bonded to at
least one surface of said fibrous layer a fire
resistant layer comprising a fire retardant agent
selected from the group consisting of compounds which
exhibit a "net endothermic effect" in a matrix

35 comprised of one or more relatively high char yield
resins. As used herein, a compound which exhibits a
"net endothermic effect" is one which absorbs heat
when exposed to fire or heat as measured by

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differential scanning calorimetry or in other words,
the summation of all endothermic and exothermic
effects generated during such exposure results in a
5   net endothermic effect or heat absorption.

        Several advantages flow from this invention. The
composition of this invention exhibits improved
resistance to ignition under the Torch Test, and low
emmission of smoke and toxic gases under the Boeing
10   BSS7238 Test and the Boeing BSS7239 Test,
respectively, as compared to a composite of equal or
substantially equal areal density formed from the
fibers of the fibrous layer alone. At the same time,
the composite of this invention exhibits ballistic
15   properties which are at the same level or
substantially at the same level of a fibrous layer
composite of the same areal density. The composite
of this invention preferably retains at least about
50% of its ballistic properties and at least about
20   50% of its mechanical properties after the Torch Test.

                BRIEF DESCRIPTION OF THE DRAWINGS

        The invention will be more fully understood and
25   further advantages will become apparent when
reference is made to the following detailed
description of the invention and the accompanying
drawings in which:
        FIG. 1 is a fragmentary view in cross-section of
30   a composite of this invention showing its essential
elements of a fibrous layer and a fire retardant
layer.
        FIG. 2 is a fragmentary view in cross-section of
a modified embodiment of this invention showing a
35   fibrous layer having a fire retardant layer bonded to
each of its parallel planar sufaces.
        FIG. 3 is a fragmentary view in cross-section of

a modified embodiment of this invention which
includes a rigid hard impact layer.

FIG. 4 is a fragmentary view in cross-section of
5 an embodiment of this invention having multiple fire
retardant layers.

DETAILED DESCRIPTION OF THE INVENTION

10   The ballistic resistant article of this invention
exhibits several beneficial properties. For example,
the ballistic resistant article has reduced smoke
production when evaluated in the smoke test of
BSS7238 using an optical density, "D_S", measurement
15 at 4.0 minutes which is generally equal to or less
than about 500, preferably equal to or less than
about 200, more preferably equal to or less than
about 80 and most preferably equal to or less than
about 50.

20   The ballistic performance of the article of this
invention is not significantly impaired after
subjection to heat and/or flame. The ballistic
performance of the article during ballistic impact
can be expressed in terms of specific energy
25 absorption (SEA). The specific energy absorbed
during a ballistic impact can be calculated based on
the areal density (AD) using the following equation:

$$SEA(Jm^2/kg) = 1/2 \ [mv^2/AD]$$

30
where
        m is mass of the projectile;
        v is velocity of the projectile which is
statistically at the borderline of complete
35 penetration (i.e. the projectile velocity which has a
50% probability of penetrating the target);and
        AD is the areal density of the ballistic
resistant article, and is the weight of the article

per unit area, kg/m^2.

The SEA of the ballistic resistant article of this invention prior to subjection to the Torch test (see the examples) is generally at least about 30% of the SEA of a ballistic amor of the same areal density consctruted form the fibrous layer. The SEA of the article of this invention is preferably about 75%, more preferably about 80%, and most preferably about 90% of the SEA of a ballistic armor of the same areal denisty constructed from the fibrous layer alone. In those embodiments of choice, the SEA is from about 95 to about 100% of the SEA of a ballistic armor of the same areal density constructed from the fibrous layer alone.

The article of this invention also retains significant portions of its ballistic resistance after subjection to the Torch Test. For example, after subjection to the Torch Test, the reduction in SEA is general not more than about 90%, preferably not more than about 50%, more preferably not more than about 30% and most preferably not more than about 10%, with those embodiments in which the reduction in SEA is not more than about 1% being the embodiments of choice.

The fibers in the fibrous layer of the ballistic resistant article of this invention also retain their tensile properties after subjection to the Torch Test as measured by ASTM D3039. For example, the fibers retain at least about 20%, preferably at least about 40%, more preferably at least about 60% and most preferably at least about 80% of their tensile properties, with those embodiments with at least about a 95% retention of tensile properties being the embodiments of choice.

The present invention will be better understood by those of skill in the art by reference to the figures. Referring to FIGs. 1 and 2, the numeral 10

indicates a ballistic resistant article 10. In its
broadest aspects, article 10 as depicted in FIG. 1
comprises at least two layers, one of which in
5 fibrous layer 12 and the other of which is flame
resistance layer 14.

The combined areal density of fibrous layer(s) 12
and flame resistant layer(s) 14 may vary widely. In
general, the areal density is equal to or greater
10 than about 1.0 Kg/m^2. In the preferred embodiments
of the invention, the areal density is equal to or
greater than about 2.0 Kg/m^2, and in the more
preferred embodiments of the invention, the areal
density is from about 1 to about 100 Kg/m^2· In the
15 most preferred embodiments of the invention, the
areal density is from about 2 to about 100 Kg/m^2.

The volume percents of fibrous layer(s) 12 and
flame resistant layer(s) 14 in article 10 may vary
widely. In general, the volume percent of fibrous
20 layer(s) 12 may vary from about 50 to about 99 volume
percent, and the volume percent of flame resistant
layer(s) 14 may vary from about 1 to about 50 weight
percent based on the total weight of article 10. In
the preferred embodiments of the invention, the
25 volume percent of fibrous layer(s) 12 may vary from
about 85 to about 99 volume percent, and the volume
percent of the flame resistant layers from about 1 to
about 15 volume percent based on the total volume of
article 10. In the more preferred embodiments of the
30 invention, the volume percent of fibrous layer(s) 12
may vary from about 90 to about 96 volume percent and
the volume percent of flame resistant layer(s) 14 may
vary from about 4 to about 10 volume percent based on
the total volume of article 10, and in the most
35 preferred embodiments of the invention, the volume
percent of fibrous layer(s) 12 may vary from about 93
to about 96 volume percent and the volume percent of
flame resistant layer(s) 14 may vary from about 4 to

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about 7 weight percent on the aforementioned basis.

Fibrous layer 12 comprises a network of fibers in
a matrix. For purposes of the present invention,

5   fiber is defined as an elongated body, the length
dimension of which is much greater than the
dimensions of width and thickness. Accordingly, the
term fiber as used herein includes a monofilament
elongated body, a multifilament elongated body, a

10   multifilament elongated body, a ribbon, a strip, a
film and the like having regular or irregular cross
sections. The term fibers includes a plurality of
any one or combination of the above.

The cross-section of fibers for use in this

15   invention may vary widely. Useful fibers may have a
circular cross-section, a oblong cross-section or an
irregular or regular multi-lobal cross-section having
one or more regular or irregular lobes projecting
from the linear or longitudinal axis of the fiber.

20   In the particularly preferred embodiments of the
invention, the fibers are of substantially circular
or oblong cross-section and in the most preferred
embodiments are of circular of substaintially
circular cross-section.

25   In article 10 of this invention, the fibers may
be arranged in networks having various
configurations. For example, a plurality of fibers
can be grouped together to form twisted or untwisted
yarn or fiber bundles in various alignments. The

30   fiber or yarn may be formed as a felt, knitted or
woven (plain, basket, satin and crow feet weaves,
etc.) into a network, fabricated into non-woven
fabric, arranged in parallel array, layered, or
formed into a woven fabric by any of a variety of

35   conventional techniques. Among these techniques, for
ballistic resistance applications we prefer to use
those variations commonly employed in the preparation
of aramid fabrics for ballistic-resistant articles.

For example, the techniques described in U.S. Patent
NO. 4,181,768 and in M.R. Silyquist et al., J.
Macromol Sci. Chem., A7(1), pp. 203 et. seq. (1973)
5   are particularly suitable. In preferred embodiments
of the invention, the fibers in each layer 12 are
aligned in a substaintially parallel and
unidirectional fashion, and the matrix material
substantially coats the individual filaments. Such
10   preferred fiber configurations are described in more
detail in Patent Nos. 4,623,574; 4,748,064;
4,916,000,; 4,403,012; 4,457,985; 4,650,710;
4,681,792; 4,737,401; 4,543,286; 4,563,392; and
4,501,856.

15   The type of fibers used in the fabrication
fibrous layer 12 of the article of this invention may
vary widely. Preferred fibers for use in the
practice of this invention are those having a
tenacity equal to or greater than about 7 g/d (as
20   measured by an Instron Tensile Tester), tensile
modulus equal to or greater than about 130 g/d (as
measured by an Instron Tensile) and an
energy-in-break equal to or greater than about 30
joules/gram. Particularly preferred fibers are those
25   having a tenacity equal to or greater than about 20
g/d, a tensile modulus equal to or greater than about
500 g/d and energy-in-break equal to or greater than
about 30 joules/grams. Amongst these particularly
preferred embodiments, most preferred are those
30   embodiments in which the tenacity of the fibers are
equal to or greater than about 25 g/d, the tensile
modulus is equal to or greater than about 1000 g/d,
and the energy-to-break is equal to or greater than
about 35 joules/grams. In the practice of this
35   invention, fibers of choice have a tenacity equal to
or greater than about 30 g/d, a tensile modulus equal
to or greater than about 1300 g/d and an
energy-to-break is equal to or greater than about 40

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joules/grams.

The denier of the fiber may vary widely. In
general, fiber denier is equal to or less than about
4000. In the preferred embodiments of the invention,
fiber denier is from about 10 to about 4000, in the
more preferred embodiments of the invention fiber
denier is from about 50 to about 3500 and in the
mmost preferred embodiments of the invention, fiber
denier is from about 100 to about 3000.

Fibers for use in the practice of this invention
may be inorganic fibers, organic fibers or a
combination thereof. Useful inorganic fibers include
S-glass fibers, E-glass fibers, boron fibers,
S_2-glass fibers, alumina-silica fibers,
zirconia-silica fibers, carbon fibers and the like.
Illustrative of useful organic fibers are those
composed of polyesters, polyolefins, polyetheramides,
fluoropolymers, polyethers, celuloses, phenolics,
polyesteramides, polyurethanes, epoxies,
amimoplastics, silicones, polysulfones,
polyetherketones, polyetheretherketones,
polyurethanes, polyesterimides, polyphenylene
sulfides, polyether acryl ketones, poly(amideimides),
and polyimides. Illustrative of other useful organic
filaments are those composed of aramids (aromatic
polyamides), such as poly(m-xylylene adipamide), poly
(p-xylylene sebacamide), (poly
2,2,2-trimethylhexamethylene terephthalamide), poly
(hexamethylene terephthalamide), poly (metaphenylene
isophthalamide) (Nomex®) and poly (p-phenylene
terephthalammide) (Kevlar®); aliphatic and
cycloaliphatic polyamides, such as a copolyamide of
30% hexamethylene diammonium isophthalate and 70%
hexamethylene diammonium adipate, the copolyamide of
up to 30% bis-(-amidocyclohexyl)methylene,
terephthalic acid and caprolactam, polyhexamethylene
adipamide (nylon 66), poly(butyrolactam) (nylon 4),

poly (9-aminonoanoic acid) (nylon 9),
poly(enantholactam) (nylon 7), poly(capryllactam)
(nylon 8), polycaprolactam (nylon 6), poly
5 (butamethylene adipamide)(nylon 4, 6),
polyhexamethylene sebacamide (nylon 6, 10),
polyaminoundecanamide (nylon 11), polydodecamide
(nylon 12), polyhexamethylene isophthalamide,
poly(nonamethylene azelamide) (nylon 9,9),
10 poly(decamethylene azelamide) (nylon 10,9),
poly(decamethylene sebacamide) (nylon 10,10),
poly([bis-(4-aminocyclothexyl) methane 1,10-
decanedicarboxamide] (Qiana) (trans), or combinations
thereof; and aliphatic, cycloaliphatic and aromatic
15 polyesters such as poly(1,4-cyclohexylidene dimethyl
eneterephathalate) cis and trans, poly(ethylene-1,
5-naphthalate), poly(ethlene-2,6-naphthalate),
poly(1,4-cyclohexane dimethylene terephthalate)
(trans),poly(decamethylene terephthalate),
20 poly(ethylene terephthalate), poly(ethylene
isophthalate), poly(ethylene oxybenozoate),
poly(para-hydroxy benzoate),
poly(dimethylpropiolactone), poly (decamethylene
adipate), poly(ethylene succinate), poly(ethylene
25 azelate), poly(decamethylene sebacate), poly(2,2
-dimethylpropiolactone), and the like.
      Also illustrative of useful organic fibers are
those of liquid crystalline polymers such as
lyotropic liquid crystalline polymers which include
30 polypeptides such as polyγ-benzyl L-glutamate and the
like; aromatic polyamides such as poly
(1,4-benzammide), poly(chloro-1,4-phenylene
terephthalamide), poly(1,4-phenylene fumaramide),
poly(chloro-1,4-phenylene fumaramide), poly-
35 (4,4'-benzanilide trans, trans-muconamide), poly-
(1,4-phenylene mesaconamide), poly(1,4-phenylene-
trans-1,4-cyclohexylene amide), poly
(chloro-1,4-phenylene-trans-1,4-cyclohexylene amide),

poly(chloro-1,4-phenylene) (trans-1,4-cyclohexylene
amide), poly(1,4-phenylene
1,4-dimethyl-trans-1,4-cyclohexylene amide),

5   poly(1,4-phenylene 2,5-pyridine amide),
poly(chloro-1,4-phenylene 2,5-pyridine amide), poly
(3,3'-dimethyl-4,4'- biphenylene 2,5 pyridine amide),
poly (1,4-phenylene 4,4'-stilbene amide),
poly(chloro-1,4-phenylene 4,4'-stilbene amide), poly

10   1,4-phenylene 4,4'-azobenzene amide), poly
(4,4'-azobenzene 4,4'-azobenzene amide),
poly(1,4-phenylene 4,4'-azoxybenzene amide),
poly(4-4-azobenzene 4,4'-azoxybenzene amide), poly
(1,4- cyclohexylene 4,4'-azabenzene amide), poly

15   4,4'-azobenzene terephthal amide), poly-
(3,8-phenanthridinone terephthal amide),
poly(4-4'-biphenylene terephthal amide),
poly(4,4'-bibenzo amide), poly(1,4-phenylene-
4,4'-bibenzo amide), poly (1,4-phenylene-

20   4,4'-terephenylene amide), poly(1,4-phenlene-
2,6-naphthal amide), poly(1,4-phenylene
4,4'-terephenylene amide), poly (1,4-phenylene-
2,6-naphthalamide), poly(1,5-naphthylene terephthal
amide), poly (3,3'-dimethyl-4,4-biphenylene

25   terephthal amide), poly(3,3'-dimethoxy-4,4'
-biphenylene terephthal amide),
poly(3,3'-dimethoxy-2,2-biphenylene 4,4-bibenzo
amide) and the like; polyoxamides such as those
derived from 2,2-dimethyl-4,4' diamino biphenyl and

30   chloro-1,4-phenylene diamine; polyhydrazides such as
poly(chloroterephthalic hydrazide), poly(
2,5-pyridine dicarboxylic acid hydrazide)
poly(terephthalic hydrazide),
poly(terephthalic-chloroterephthalic hydrazide) and

35   the like; poly(amide-hydrazides) such as
poly(terephthaloyl 1,4 amino-benzhydrazide) and those
prepared from 4-amino-benzhydrazide, oxalic
dihydrazide, terephthalic dihydrazide and

para-aromatic diacid chlorides; polyesters such as
poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-
cyclohexylenecarbonyl-β-oxy-1,4-phenyl-eneoxyterephtha
5   loyl) and poly (oxy-cis-
1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylencar
bonyl-β-oxy-1,4-phenyleneoxyterephthaloyl) in
methylene chloride-o-cresol, poly
[(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyc
10   clohexylenoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-
β-oxy (2-methyl-1,3-phenylene) oxyterephthaloyl] in
o-chlorophenol and the like; polyazomethines such as
those prepared from 4,4'-phenylendiamine and
terephthalaldelyde and the like; polyisocyanides such
15   as poly (γ-phenyl ethyl isocyanides) poly (n-octyl
isocyanides), and the like; polyisocyanates such as
poly(n-alkyl isocyanates) as for example poly(n-butyl
isocyanate), poly(n-hexyl isocyanate) and the like;
lyrotropic crystalline polymers with heterocylic
20   units such as poly(1,4-phenylene-2,
6-benzobisthiazole) (PBT), poly(1,4-phenylene-2,6-
benzobisthiazole)(PBO), poly(1,4-phenylene
-1,3,4-oxadiazole), poly(1,4-phenylene
-2,6-benzobisimidazole), poly[2,5(6)-benzimidazole]
25   (AB-PBI), poly-[2,6-
(1,4-phenylene)-4-phenylquinoline],
poly-[1,1'-(4,4-biphenylene)-6,6'bis(4-phenylquinoline
)] and the like; polyorganophosphazines such as
polyphosphazine, polybisphenoxyphosphazine,
30   poly[bis(2,2,2'-tirifluoroethyelene) phosphazine] and
the like; metal polymers such as those derived by
condensation of trans-bis-(tri-n-butylphosphine)
platinum dichloride with a bisacetylene or
trans-bis-(tri-n-butylphoshine)bis(1,4-butadinynyl)
35   platinum and similar combinations in the presence of
suprous iodine and an amide; cellulose and cellulose
derivatives such as esters of cellulose as for
example triacetate cellulose, acetate cellulose,

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acetate-butyrate cellulose, nitrate cellulose, and
sulfate cellulose, ethers of cellulose as for
example, ethyl ether cellulose, hydroxymethyl ether
5   cellulose, hydroxypropyl ether cellulose,
hydroxymethyl ether cellulose, hydroxpropyl ether
cellulose, carboxymethyl ether cellulose, ethyl
hydroxyethyl ether cellulose, cyanoethylethyl ether
cellulose, ether-esters of cellulose as for example
10 acetoxyethyl ether cellulose and benzoyloxpropyl
ether cellulose; and thermotropic liquid crystalline
polymers such as celuloses and their derivations as
for example hydyroxpropyl cellulose, ethyl cellulose
propionoxpropyl cellulose, thermotropic liquid
15 crystalline polymers such as celluloses and their
derivatives as for example hydroxy propyl cellulose
and propionoxy-propyl allulose, thermotropic
copolyesters as for example copolymers of
6-hydroxy-2-naphthoic acid and p-hydroxy benzoic
20 acid, copolymers of 6-hydroxy-2-naphthoic acid,
terephthalic acid and p-amino phenol, copolymers of
6-hydroxy-2-naphthoic acid, terephthalic acid and
hydroquinone, copolymers of 6-hydroxy-2-naphthoic
acid, p-hydroxy benzoic acid, hydroquinone and
25 terephthalic acid, copolymers of 2,6-napthalene
dicarboxylic acid, terephthalic acid, isophthalic
acid and hydroquinone, copolymers of 2,6-naphthalene
dicarboxylic acid and terephthalic acid, copolymers
of p-hydroxybenzoic acid, terephthalic acid,
30 4,4'-dihydroxydiphenyl, copolymers of
p-hydroxybenzoic acid, terephthalic acid, isophthalic
acid and 4,4'-dihydroxydiphenyl, p-hydroxybenzoic
acid, isophthalic acid, hydroquinone and
4,4'-dihydroxbenzophenone, copolymers of
35 phenylterephthalic acid and hydroquinone, copolymers
of chlorohydroquinone, terephthalic acid and ethylene
dioxy-4,4'-dibenzoic acid, copolymers of
hydroquinone, methylhydroquinone, p-hydroxybenzoic

acid and isophthalic acid, copolymers of
(1-phenylethyl) hydroquinone, terephthalic acid and
hydroquinone, and copolymers of poly(ethylene

5   terephthalate) and p-hydroxybenzoic acid;
thermotropic polyamides; and thermotropic copoly
(amide-esters).

     Also illustrative of useful organic fibers for
use in the fabrication of fibrous layer 12 are those

10 composed of extended chain polymers formed by
polymerization of α,β-unsaturated monomers of the
formula:

$$R_1R_2-C = CH_2$$
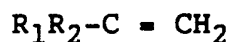
15

wherein:

     R_1 and R_2 are the same or different and are
hydrogen, hydroxy, halogen, alkylcarbonyl, carboxy,
alkoxycarbonyl, heterocycle or alkyl or aryl either

20 unsubstituted or substituted with one or more
substituents selected from the group consisting of
alkoxy, cyano, hydroxy, alkyl and aryl. Illustrative
of such polymers of α,β-unsaturated monomers are
polymers including polystyrene, polyethylene,

25 polypropylene, poly(1-octadecene), polyisobutylene,
poly(1-pentene), poly(2-methylstyrene),
poly(4-methylstyrene), poly(1-hexene),
poly(1-pentene), poly(4-methylpentene), poly
(1-butene), polyvinyl chloride, polybutylene,

30 polyacrylonitrile, poly(methyl pentene-1), poly(vinyl
alcohol), poly(vinyl-acetate), poly(vinyl butyral),
poly(vinyl chloride), poly(vinylidene chloride),
vinyl chloride-vinyl acetate chloride copolymer,
poly(vinylidene fluoride), poly(methyl acrylate,

35 poly(methyl methacrylate), poly(methacrylo-nitrile),
poly (acrylamide), poly(vinyl fluoride), poly(vinyl
formal), poly(3-methyl-1-butene), poly(1-pentene),
poly(4-methyl-1-butene), poly(1-pentene),

pol(4-methyl-1-pentence, poly(1-hexane),
poly(5-methyl-1-hexene), poly(1-octadecene),
poly(vinyl-cyclopentane), poly(vinylcyclothexane),
poly(viny-ethylether), poly(vinyl methyl ether),
poly(vinyl-ethylether), poly(vinyl propylether),
poly(vinyl carbazole), poly(vinyl prolidone),
poly(2-chlorostyrene), poly(4-chlorostyrene),
poly(vinyl formate), poly(vinyl butyl ether),
poly(vinyl octyl ether), poly(vinyl methyl ketone),
poly(methyl-isopropenyl ketone),
poly(4-phenylstyrene) and the like.

In the most preferred embodiments of this
invention, the fibers forming fibrous layer(s) 12 are
"flammable fibers". As used herein, "flammable
fibers" are those which are ignitable when subject to
flame in the Torch Test described in the Examples
and/or which produce smoke and/or toxic gases when
subject to heat or flame such that the concentration
of the gases carbon monoxide (CO), nitrogen dioxide
(NO_2), sulfur dioxide (SO_2), hydrogen chloride (HCl),
hydrogen fluoride (HF) and/or hydrogen cyanide (HCN)
exceed the limits of BSS7239 and/or smoke reduction
is greater than 500 when evaluated in the smoke test
of BSS 7238 using an optical density "Ds" of 4.0
minutes.

Flammable fibers are preferred for use in the
practice of this invention because they may best
utilize the benefits of flame resistance layer(s)
14. Preferred flammable fibers include high
molecular weight polyethylene fibers, high molecular
weight polyethylene fibers, high molecular weight
polypropylene fibers, a high molecular weight
polyvinyl alcohol fibers, a high molecular weight
polyacrylonitrile fibers or mixtures thereof. USP
4,457,985 generally discusses such high molecular
weight polyethylene and polypropylene fibers, and the
disclosure of this patent is hereby incorported by

reference to the extent that it is not inconsistent
herewith. In the case of polyethylene fibers
preferred fibers are those of molecular weight of at

5 least 150,000, preferably at least one million and
more preferably between two million and five
million. Such extended chain polyethylene (ECPE)
fibers may be grown in solution as described in U.S.
Patent No. 4,137,394 or U.S. Patent No. 4,356,138 or

10 a fiber spun from a solution to form a gel structure,
as described in German Off. 3,004,699 and GB
2051667, and especially described in Patent No.
4,551,296 (see EPA 64,167, published Nov. 10,
predominantly linear polyethylene material that may

15 contain minor amounts of chain branching or
comonomers not exceeding 5 modifying units per 100
main chain carbon atoms, and that may also contain
admixed therewith not more than about 50 wt% of one
of more polymeric additives such as

20 alkene-1-polymers, in particular low density
polyethylene, polypropylene or polybutylene,
copolymers containing mono-olefins as primary
monomers, oxidized polyolefins, graft polyolefin
copolymers and polyoxymethylenes, or low molecular

25 weight additives such as anti-oxidants, lubricants,
ultra-violet screening agents, colorants and the like
which are commonly incorporated by reference.
Depending upon the formation technique, the draw
ratio and temperatures, and other conditions, a

30 variety of properties can be imparted to these
fibers. The tenacity of the fibers should be at
least 15 grams/denier, preferably at least about
about 25 grams/denier and most preferably at least
about 30 grams/denier. Similarly, the tensile

35 modulus of the filaments, as measured by an Instron
tensile testing machine, is at least about 300
grams/denier, preferably at least about 500
grams/denier and more preferably at least 1,000

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grams/denier and most preferably at least about 1,200
grams/denier. These highest values for tensile
modulus and tenacity are generally obtainable only by
5 employing solution grown or gel fibers processes.

Similarly, high oriented polypropylene of
molecular weight at least about 200,000 preferably at
least about one million and more preferably at least
about two million may be used. Such high molecular
10 weight polypropylene may be formed into reasonably
well oriented fibers by the techniques prescribed in
the various references referred to above, and
especially by the technique of U.S. Patent No.
4,551,296. Since polypropylene is a much less
15 crystalline material than polyethylene and contains
pendant methyl groups, tenacity values achievable
with polypropylene are generally substantially lower
than the corresponding values for polyethylene.
Accordingly, a suitable tenacity is at least about 8
20 grams/denier, with a preferred tenacity being at
least about 11 grams/denier. The tensile modulus for
polypropylene is at least about 160 grams/denier,
preferably at least about 200 grams/denier. The
particularly preferred ranges for the above-described
25 parameters can advantageously provide improved
performance in the final article.

High molecular weight polyvinyl alcohol fibers
having high tensile modulus are described in USP
4,440,711 which is hereby incorporated by reference
30 to the extent it is not inconsistent herewith. In
the case of polyvinyl alcohol (PV-OH), PV-OH fiber of
molecular weight of at least about 200,000.
Particularly useful Pv-OH fiber should have a modulus
of at least about 300 g/d, a tenacity of at least
35 about 7 g/d (preferably at least about 10 g/d, more
preferably at about 14 g/d, and most preferably at
least about 14 g/d, and most preferably at least
about 17 g/d), and an energy-to-break of at least

about 8 joules/gram are more useful in producing a
ballistic resistant article. PV-OH fibers having
such properties can be produced, for example, by the
5   process disclosed in U.S. Patent No. 4,599,267.

In the case of polyacrylonitrile (PAN), PAN
fibers of molecular weight of at least about
400,000. Particularly useful PAN fiber should have a
tenacity of at least about 10 g/d and an
10 energy-to-break of at least about 15 to about 20 g/d
and an energy-to-break of at least about 8
joules/gram is most useful in producing ballistic
resistant articles. Such fibers are disclosed, for
example, in U.S. 4,535,027.

15 The fibers are dispersed in a continuous phase of
a matrix material which preferably substantially
coats each fiber contained in the bundle of
filament. The manner in which the fibers are
dispersed may vary widely. The fibers may be aligned
20 in a substantially parallel, unidirectional fashion,
or fibers may be aligned in a multidirectional
fashion with fibers at varying angles with each
other. In the preferred embodiments of this
invention, fibers in each layer 12 are aligned in a
25 substantially parallel, unidirectional fashion such
as in a prepreg, pultruded sheet and the like.

The matrix material employed in the practice of
this invention comprises one or more "thermosetting
resins", one or more "thermoplastic resins", or a
30 combination thereof which preferably result in
relatively high char yield (preferably equal to or
greater than about 20% by weight, more preferably
from about 25 to about 80% by weight and most
preferably from about 50 to about 70% by weight based
35 on the total initial weight of the resin, when a 15mg
sample is heated at a rate of 20°C/min in an Argon
atmosphere from about room temperature (20 to 30°C)
to about 1000°C in a thermal gravimetric analyzer

(TGA). As used herein "thermoplastic resins" are
resins which can be heated and softened, cooled and
hardened limitless time without undergoing a basic
5   alteration, and "thermosetting resins" are resins
which do not tolerate thermal cycling and which
cannot be resoftened and reworked after molding,
extruding or casting and which attain new,
irreversible properties when one set at a temperature
10   which is critical to each resin.

    The choice of any thermosetting resin,
thermoplastic resin or combination for use in the
formation of the matrix may vary widely depending on
the desired characteristics of the composite. One
15   important characteristic of the matrix material is
its modulus which is preferably equal to or greater
than about 500 psi (3,450 kPa). The upper limit for
the modulus is not critical and usually the higher
the modulus the more desirable are composite
20   properties. In the preferred embodiments of the
invention, the matrix material is selected such that
the matrix material has a modulus equal to or greater
than about 500 psi (3,450 kPa), and in the
particularly preferred embodiments, these resins are
25   selected such that the matrix material has a modulus
equal to or greater than about 2,000 psi (13,800
kPa). In the most preferred embodiments of the
invention, the thermoplastic and thermosetting resins
are selected such that the matrix material has a
30   modulus equal to or greater than about 5,000 psi
(34,5000 kPa).

    Thermosetting resins useful in the practice of
this invention may vary widely. Illustrative of
useful thermosetting resins are alkyds such as those
35   derived from esterification of polybasic acids, as
for example, phthalic anhydride, fumaric acid, maleic
anhydride, isophthalic acid, terephthalic acid,
trimesic acid, hemimellitic acid, succinic

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anyhydride, fatty acids derived from mineral or
vegetable oils and the like, and polyhydric alcohols
as for example glycerol, ethylene glycol, propylene
5   glycol, pinacol, 1,4-butanediol, 1,3-propandediol,
sorbitol, pentaerythritol, 1,2-cyclohexanediol and
the like. Other useful thermosetting resins are
acrylics such as crosslinkable polyacrylics,
polyacrylates, epoxdiacrylates, urethane diacrylates
10   and the like. Still other useful thermosetting
resins are amino resins derived from reaction between
formaldehyde and various amino compounds such as
melamine, urea, aniline, ethylene urea, sulfonamide,
dicyanodiamide and the like. Other useful
15   thermosetting resins include urethanes derived from
reaction between formaldehyde and various amino
compounds such as melamine, urea, aniline, ethylene
urea, sulfonamide, dicyanodiamide and the like.
Still no other useful thermosetting resins include
20   urethanes derived from reaction of polyisocyanates or
diisocyanates such as 2,6-tolylene diisocyanate,
2,4-tolylene diisocyanate, 4,4'-diphenyl-methane
diisocyanate, 4,4'-dicyclohexyl-methane diisocyanate,
4,4'-dicyclohexyl-methane diisocyanate and the like,
25   and polyols such as glycerin, ethylene glycol,
diethylene glycol, trimethylolpropane,
1,2,6-hexanetriol, sorbitol, pentaerythritol and the
like.
     Exemplary of still other thermosetting resins
30   useful in the practice of this invention are
unsaturated polyesters derived from reaction of
dibasic acids such as maleic anhydride, fumaric acid,
adipic acid, azelaic acid and the like, and dihydric
alcohols such as ethylene glycol and propylene
35   glycol, 1,3-butylene glycol, 2,3-butylene glycol,
diethylene glycol, dipropylene glycols and the like;
and silicones such as dimethyldichlorosilane and the
like;

Yet another class of useful thermosetting resins
are epoxies based on saturated or unsaturated
aliphatic, cycloaliphatic, aromatic and heterocyclic
epoxides. Useful epoxides include glycidyl ethers
derived from epichlorohydrin adducts and polyols,
particularly polyhydric phenols. Another useful
epoxide is the diglycidyl ether of bisphenol A.
Additional examples of useful polyepoxides are
resorcinol diglycidyl ether, 3,4-epoxy-6-
methylcyclohexylmethyl-9,10-epoxystearate,
1,2-bis(2,3-epoxy-2-methylpropoxy) ethane, diglycidyl
ether of 2,2-(p-hydroxyphenyl) propane, butadine
dioxide, dicyclopentadiene dioxide, pentaerythritol
tetrakis(3,4- epoxycyclohexanecarboxylate),
vinylcyclohexene dioxide, divinylbenzene dioxide,
1,5-pentadiol bis(3,4-epoxycyclo-hexane carboxylate),
ethylene glycol bis(3,4-epoxycyclo-hexane
carboxylate), 2,2-diethyl-1,1,3-propanediol
bis(3,4-epoxycyclohexanecarboxylate), 1,6-hexanediol
bis(3,4-epoxycyclohexanecarboxylate),
2-butene-1,4-diol trimethylolpropane tris
(3,4-expoxy-6-methylcyclohexanecarboxylate),
1,1,1-trimethylolpropane tris (3,4-
expoxycyclohexanecarboxylate), 1,2,3-propanetriol
tris(3,4-epoxycyclohexanecarboxylate), dipropylene
glycol bis(2-ethylhexyl-4,5-
epoxycyclohexane-1,2-dicarboxylate), diethylene
glycol bis(3,4-epoxy-6-methylcyclohexanecarboxylate),
triethylene glycol bis(3,4 -
epoxycylohexanecarboxylate),
3,4-epoxycyclohexyl-methyl
3,4-epoxycyclohexanecarboxylate,
3,4-epoxy-1-methylcyclohexylmethyl
3,4-epoxy-1-methylcyclohexane-carboxylate,
bis(3,4-epoxycyclohexylmethyl) pimelate,
bis(3,4-epoxy-6-methylenecyclohexylmethyl) maleate,
bis(3,4-epoxy-6-methylcyclohexylmethyl) succinate,

methylcyclohexylmethyl) sebacate,
bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate,
bis(3,4-epoxycyclohexylmethyl) terephthalate,

5   2,2'-sulfonyldiethanol
bis(3,4-epoxycyclohexanecarboxylate), N,N'-ethylene
bis(4,5-epoxycyclohexane-1,2-dicarboximide),
di(3,4-epoxycyclohexylmethyl)
1,3-tolylenedicarbamate,

10   3,4-epoxy-6-methylcyclohexanecarboxaldehyde acetal,
3,9-bis(3,4-epoxycylohexyl) spirobi-(methadioxane),
and the like.

       Useful thermosetting resins also include phenolic
resins produced by the reaction of phenols and

15   aldehydes. Useful phenols include phenol, o-cresol,
m-cresol, p-cresol, p-tertbutylphenol,
p-tertoctylphenol, p-nonylphenol, 2,3-xylenol,
2,4-xylenol, 2,5-xylenol, 2,6-xylenol, 3,1-xylenol,
3,4-xylenol, resorcinol, bispenol-A and the like.

20   Useful aldehydes include formaldehyde, acetaldehyde,
propionaldehyde, n-butyraldehyde, isobutyraldehyde,
glyoxal, furfural and the like.

       Other useful thermosetting resins are vinylesters
such as the condensation product of epoxide resins

25   and unsaturated acids usually diluted in a compound
having double bond unsaturation such as vinylaromatic
monomer as for example styrene and vinyltoluene, and
diallyl phthalate. Illustratrive of useful
vinylesters are diglycidyl adipate, diglycidyl

30   isophalate, di-(2,3-epoxybutyl) adipate,
di-(2,3-epoxybutyl) oxalate, di-(2,3-epoxyhexyl)
succinate, di-(3,4-epoxybutyl) maleate,
di-(2,3-epoxyhexyl) succinate, di-(3,4-epoxybutyl)
maleate, di-(2,3-epoxyoctyl) pimelate,

35   di-(2,3-epoxybutyl) phthalate, di-(2,3-epoxyoctyl)
tetrahydrophthalate, di-(4,5-epoxy-dodecyl) maleate,
di-(2,3-epoxybutyl) terephthalate,
di-(2,3-epoxypentyl) thiodipropionate,

di-(5,6-epoxy-dodecyl)maleate, di-(2,3-epoxybutyl)
terephthalate, di-(2,3-epoxyoctyl)
tetrahydrophthalate, di-(4,5-epoxy-dodecyl) maleate,
5 di-(2,3-epoxybutyl) terephthalate,
di-(2,3-epoxypentyl) thiodipropionate,
di-5,6-epoxy-tetradecyl) diphenyldicarboxylate,
di-(3,4-epoxyheptyl) sulphonyldibutyrate,
tri-(2,3-epoxybutyl) 1,2,4 butanetricarboxylate,
10 di-(5,6-epoxypentadecyl) maleate, di-(2,3-epoxybutyl)
azelate, di(3,4-epoxypentadecyl) citrate,
di-(5,6-epoxyoctyl) cyclohexane-1,3-dicarboxylate,
di-(4,5-epoxyoctadecyl) malonate, bisphenol-A-fumaric
acid polyester and the like.
15   Preferred thermosetting resins for use in the
practice of this invention are vinyl esters,
unsaturated polyesters, epoxies, phenolics. and
mixtures thereof. Particularly preferred
thermosetting resins are vinyl esters, epoxies and
20 phenolics, with vinylesters being the thermosetting
resin of choice.
        Thermoplastic resins for use in the practice of
this invention may also vary widely and may include
these mentioned hereinabove for use in the formation
25 of fibrous layer 12. Illustrative of useful
thermoplastic resins are polylactones such as
poly(pivalolactone), poly (caprolactone) and the
like; polyurethanes derived from reaction of
diisocyanates such as 1,5-naphalene diisocyanate,
30 p-phenylene diisocyanate, m-phenylene diisocyanate,
2,4-toluene diisocyanate, 4,4'-diphenylmethane
diisocyanate, 3',3-dimethyl-4,4'diphenylmethane
diisocyanate, 3,3' dimethyl-4,4' biphenyl
diisocyanate, 4,4' diphenylisopropylidene
35 diisocyanate, 3,3'-dimethyl-4,4' diphenyl
diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane
diisocyanate, dianisidine diisocyanate, tolidine
diisocyanate, hexamethylene diisocyanate,

4,4'-diisocyanadodiphenylmethane and the like and
linear long-chain diols such as poly(tetramethylene
adipate), poly(ethylene adipate), poly(1,4-butylene
adipate), poly(1,5-pentylene adipate),
poly(1,3-butylene adipate), poly(ethylene adipate),
poly(1,4-butylene adipate), poly(1,5-pentylene
adipate), poly(1,3-butylene adipate), poly(ethylene
succinate), poly(2,3-butylene succinate), polyether
diols and the like; polycarbonates such as
poly[methane bis-(4-phenyl) carbonate],
poly[1,1-ether bis(4-phenyl) carbonate],
poly[1,1-cyclohexane bis(4-phenyl) carbonate] and
the like; polysulfones; polyether ether ketones;
polyamides such as poly(4-amino butyric acid),
poly(hexamethylene adipamide), poly(6,aminohexanoic
acid), poly(m-xylylene adipamide), poly(p-xylylene
sebacamide), poly(2,2,2-trimethyl hexamethylene
terephthalamide), poly(metaphenyleneisophthalamide)
(Nomex®), poly(p-phenylene terephthalamide)
(Kevlar®), and the like; polyesters such as
poly(ethylene azelate),
poly(ethylene-1,5-naphthalate), poly(1,4-cyclohexane
dimethylene terephthalate), poly(ethylene
oxybenzoate) (A-Tell), poly(para-hydroxy benzoate)
(Ekonol), poly(1,4-cyclohexylidene dimethylene
terephthalate) (Kodel) (as), poly(1,4-cyclohexylidene
dimethylene terephthalate) (Kodel)(trans),
polyethylene terephthalate, polybutylene
terephthalate and the like; poly(arylene oxides) such
as poly(2,6-diphenyl-1,4-phenylene oxide) and the
like; poly(arylene sulfides) such as poly(phenylene
sulfide) and the like; polyetherimides; thermoplastic
elastomers such as polyurethane elastomers,
fluoroelastomers, butadine/acrylonitrile elastomers,
silicone elastomers, polybutadiene, polyisobutylene,
ethylene-propylene copolymers,
ethylene-propylene-diene terpolymers,

polychloroprene, polysulfide elastomers, block
copolymers, made of segments of glassy or crystalline
blocks such as polystyrene, poly(vinyl-toluene), and

5   poly(t-butyl styrene) and elastomeric blocks such as
polybutadiene, polyisoprene, ethylene-propylene
copolymers, and ethylene-propylene copolymers,
ethylene-butylene copolymers, polyether ester and the
like as for example the polystyrene-

10 polybutadiene-polystyrene block copolymer
manufactured by Shell Chemical Company under the
trade name of Kraton®; vinyl polymers and their
copolymers such as polyvinyl acetate, polyvinyl
alcohol, polyvinyl chloride, polyvinyl butyral,

15 polyvinylidene chloride, ethylene-vinyl acetate
copolymers, and the like; polyacrylics, polyacrylate
and their copolymers such as poly(ethylacrylate),
poly(n-butyl acrylate), poly(methyl methacrylate),
poly(ethyl methacrylate), poly(n-butyl methacrylate),

20 poly(n-propyl methacrylate), poly(acrylamide),
poly(acrylonitrile), poly(acrylic acid), ethylene
acrylic acid copolymers, methyl methacrylate styrene
copolymers, ethylene ethyl acrylate copolymers,
methacrylated butadiene styrene copolymers and the

25 like; polyolefins such as low density polyethylene,
polypropylene, chlorinated low density polyethylene,
poly(4-methyl-1-pentene) and the like; ionomers; and
poly(epichlorohydrins).
        In the preferred embodiments of the invention,

30 the thermoplastic material is selected from the group
consisting of polyurethanes, polyvinyls,
butadiene/olefin copolymers such as
polystyrene-polyisoprene-polystyrene block copolymer
thermoplastic elastomers, polyacrylics and

35 polyolefins. In the particularly preferred
embodiments of the invention the preferred
thermoplastic material is a polyurethane, or a
butadienes/olefin copolymer.

The proportion of matrix to fiber in fibrous
layer(s) 12 is not critical and may vary widely
depending on a number of factors including, whether
5 the matrix material has any ballistic-resistant
properties of its own (which is generally not the
case) and upon the rigidity, shape, heat resistance,
wear resistance, flammability resistance, mold cycle
time, handling characteristics and other properties
10 desired for the composite article. In general, the
proportion of matrix to fiber in the composite may
vary from relatively small amounts where the amount
of matrix is about 10% by volume of the fibers to
relatively large amounts where the amount of matrix
15 is up to about 90% by volume of the fibers. In the
preferred embodiments of this invention, matrix
amounts of from about 15 to about 85% by volume are
employed. All volume percents are based on the total
volume of the composite. In the particularly
20 preferred embodiments of the invention,
ballistic-resistant articles of the present invention
contain a relatively minor proportion of the matrix
(e.g., about 10 to about 30% by volume of composite),
since the ballistic-resistant properties are almost
25 entirely attributable to the fiber, and in the
particularly preferred embodiments of the invention,
the proportion of the matrix in the composite is from
about 10 to about 30% by volume of filaments.
    Fibrous layer 12 of article 10 of this invention
30 can be fabricated using a number of procedures. In
general, layers 12 are formed by molding the
combination of the matrix material and fibers in the
desired configurations and amounts by subjecting the
combination to heat, and pressure during a mold cycle
35 time. An advantage of those embodiments of this
invention in which the thermosetting resin is a vinyl
ester is that relative short mold cycle times and
temperatures may be employed.

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The fibers may be premolded by subjecting them to
heat and pressure. For example, for extended chain
polyethylene fibers, molding temperatures range from
abut 20 to about 150°C, preferably from about 80 to
5 about 145°C, more preferably from about 100 to about
135°C depending on the type of matrix material
selected. The molding pressure may range from about
0 psi (0 kPa) to about 10,000 psi (69,000 kPa). A
pressure between about 10 psi (69 kPa) and about 100
10 psi (690 kPa), when combined with temperatures below
about 100°C for a period of time less than about 1.0
min., may be used simply to cause adjacent fibers to
stick together. Pressures from about 100 psi to
about 10,000 psi (69,000 kPa), when coupled with
15 temperatures in the range of about 100 to about 155°C
for a time of between about 1 to about 5 min.,may
cause the fibers to deform and to compress together
(generally in a film-like shape). Pressures from
about 100 psi (690 kPa) to about 10,000 psi (69,000
20 kPa), when coupled with temperatures in the range of
about 150 to about 155°C for a time of between 1 to
about 5 min., may cause the film to become
translucent or transparent. For polypropylene
fibers, the upper limitation of the temperature range
25 would be about 10 to about 20°C higher than for ECPE
filament.

In the preferred embodiments of the invention,
the fibers (premolded if desired) are precoated with
30 the desired matrix material prior to being arranged
in a network and molded as described above. The
coating may be applied to the fibers in a variety of
ways and any method known to those of skill in the
art for coating filaments may be used. For example,
35 one method is to apply the matrix material to the
stretched high modulus fibers either as a liquid, a
sticky soild or particles in suspension, or as a
fluidized bed. Alternately, the matrix material may

be applied as a solution or emulsion in a suitable
solvent which does not adversely affect the
properties of the fiber at the temperature of

5 application. In these illustrative embodiments, any
liquid capable of dissolving or dispersing the matrix
material may be used. However, in the preferred
embodiments of the invention useful solvents include
water, paraffin oils, ketones, alcohols, aromatic

10 solvents or hydrocarbon solvents or mixtures thereof,
with illustrative specific solvents including
paraffin oil, xylene, toluene and octane. The
techniques used to dissolve or disperse the matrix in
the solvents will be those conventionally used for

15 the coating of thermoplastic resins on a variety of
substrates.

Other techniques for applying the coating to the
fibers may be used, including coating of the high
modulus precursor (gel fiber) before the high

20 temperature stretching operation, either before or
after removal of the solvent from the fiber. The
fiber may then be stretched at elevated temperatures
to produce the coated filaments. The gel fiber may
be passed through a solution of the appropriate

25 matrix material, as for example an elastomeric
material dissolved in paraffin oil, or an aromatic or
aliphatic solvent, under conditions to attain the
desired coating. Crystallization of the polymer in
the gel fiber may or may not have taken place before

30 the fiber passes into the cooling solution.
Alternately, the fiber may be extruded into a
fluidized bed of the appropriate matrix material in
powder form.

The proportion of coating on the coated fibers or

35 fabrics may vary from relatively small amounts (e.g.,
1% by weight of fibers) to relatively large amounts
(e.g., 150% by weight of fibers), depending upon
whether the coating material has any impact or

ballistic-resistant properties of its own (which is
generally not the case) and upon the rigidity, shape,
heat resistance, wear resistance, flammability
5 resistance and other properties desired for the
complex composite article. In general,
ballistic-resistant articles of the present invention
containing coated fibers should have a relatively
minor proportion of coating (e.g., about 10 to about
10 30 percent by volume of fibers), since the
ballistic-resistant properties are almost entirely
attributable to the fiber. Nevertheless, coated
fibers with higher coating contents may be employed.
Generally, however, when the coating constitutes
15 greater than about 60% (by volume of fiber), the
coated fiber is consolidated with similar coated
fibers to form a simple composite.

Furthermore, if the fiber achieves its final
properties only after a stretching operation or other
20 manipulative process, e.g. solvent exchanging, drying
or the like, it is contemplated that the coating may
be applied to a precursor material of the final
fiber. In such case, the desired and preferred
tenacity, modulus and other properties of the
fibershould be judged by continuing the manipulative
25 process on the fiber precursor in a manner
corresponding to that employed on the coated fiber
precursor. Thus, for example, if the coating is
applied to the xerogel fiber described in U.S. Patent
No. 4,551,296, and the coated xerogel fiber is then
30 stretched under defined temperature and stretch
ration conditions, then the fiber tenacity and fiber
modulus values would be measured on uncoated xerogel
fiber which is similarly stretched.

It is a preferred aspect of the invention that
35 each fiber be substantially coated with the matrix
material for the production of composites having
improved impact protection, delamination resistance,

rigidity and/or ballistic resistance, and relatively
shorter mold cycle times, preferably of less than
about 30 minutes. Fibers are substantially coated by
5   using any of the coating processes described above or
can be substantially coated by employing and other
process capable or producing fiber coated essentially
to the same degree as a filament coated by the
processes described heretofore techniques (e.g., by
10 employing known high pressure molding.)

The fibers and networks produced therefrom are
formed into "simple composites" as the precursor to
preparing the complex composite articles of the
present invention. The term, "simple composite", as
15 used herein is intended to mean fibrous layer 12 made
up of one layer of fibers as described above with a
single major matrix material, which material may
include minor proportions of other materials such as
fillers, lubricants or the like.

20 The proportion of matrix material to fiber is
variable for the simple composites, with matrix
material amounts of from about 5% to about 150 vol%,
by volume of the composite, representing the broad
general range. Within this range, it is preferred to
25 use composites having a relatively high fiber
content, such as composites having only about 10 to
about 30 vol% matrix material by volume of the
composite.

Stated another way, the fiber network occupies
30 different proportions of the total volume of the
simple composite. Preferably, however, the fiber
network comprises at least about 30 volume percent of
the simple composite. For ballistic protecting, the
fiber network comprises at least about 50 volume
35 percent, more preferably about 70 volume percent, and
most preferably at least about 75 volume percent,
with the matrix occupying the remaining volume.

A particularly effective technique for preparing

a preferred simple composite comprised of substantially parallel, undirectional, aligned fibers includes the steps of pulling a fiber or bundles of
5   fibers through a bath containing a solution of a matrix material and circumferentially winding this fiber into a single sheet-like layer around a bundle of fibers the length of a suitable form, such as a cylinder. The solvent, if used, is then evaporated
10 leaving a sheet-like layer of fibers embedded in a matrix that can be removed from the cylindrical form. Alternatively, a plurality of fibers or bundles of fibers can be simultaneously pulled through the bath containing a solution or dispersion
15 of a matrix material and laid down in closely positioned, substantially parallel relaion to one another on a suitable surface. Evaporation of the solvent leaves a sheet-like layer comprised of unidirectional fibers which are coated with the
20 matrix material and which are substantially parallel and aligned along a common fiber direction. The sheet is suitable for subsequent processing such as laminating to another sheet to form fibrous layer 12 containing more than one layer of fibers.
25   Similarly, a fiber-type simple composite can be produced by pulling a group of fiber bundles through a dispersion or solution of the matrix material to substantially coat each of the individual fibers, and then evaporating the solvent to from the coated
30 fiber. The fiber can then, for example, be employed to form fabrics, which in turn, can be used to form more complex composite structures. Moreover, the coated fiber can also be processed into a simple composite by employing conventional fiber winding
35 techniques; for example, the simple compsite can have coated yarn formed into overlapping fiber layers.

        The number of layers of simple composite included in fibrous layers 12 may vary widely depending on the

use of article 10. For example, in those uses where
article 10 would be used as ballistic protection, the
number of layers would depend on a number of factors

5   including the degree of ballistic protection desired
and other factors known to those of skill in the
ballistic protection art. In general for this
application, the greater the degree of protection
desired the greater the number of simple composite

10 included in fibrous layer 12 for a given weight of
layer 12. Conversely, the lessor the degree of
ballistic protection required, the lessor the number
of simple composite layers required for a given
weight of layer 12. It is convenient to characterize

15 the geometries of layer 12 by the geometries of the
fibers and then to indicate that the matrix material
may occupy part or all of the void space left by the
network of fibers. One such suitable arrangement is
a plurality of simple composite layers in which the

20 coated fibers are arranged in a sheet-like array and
aligned parallel to one another along a common fiber
direction. Successive simple composite layers of
such coated, uni-directional fibers can be rotated
with respect to the previous layer to form a

25 laminated fibrous layer 12. An example of such
laminated fibrous layer 12 are those with the second,
third, fourth and fifth layers rotated +45°, -45°,
90° and 0°, with respect to the first layer, but not
necessarily in that order, Other examples include

30 laminated fibrous layer 12 with 0°/90° layout of yarn
of fibers. Procedures and materials for the
fabrication of such preferred fibrous layers 12 are
described in detail in U.S. Patent Nos. 4,457,985;
4,613,535; 4,748,064; 4,916,000; 4,403,012;

35 4,623,574; and 4,737,402, which are incorporated
herein by reference.

The article 10 of this invention includes one or
more fire retardant layer(s) 12 bonded to a surface

of one or more of fibrous layers 14. As used herein
a "fire retardant layer" is a continuous or
discontinuous layer comprised of a fire retardant
5 composition comprising one or more inorganic or
organic fire retardant agents which exhibit an
endothermic effect on heating in a matrix material
comprising one or more high char yield resins.

The fire retardant composition of this invention
10 exhibits several unique properties. For example, the
composition is "nonflammable". As used herein,
"inflammable" means that the composition is not
ignited when subjected to the Torch test. Another
advantage of the composition of this invention is
15 that it generates reduced levels of smoke and toxic
gases when subjected to heat in the procedures of
Boeing Specifications 7238 and 7239. In general, the
concentration levels of toxic gases, carbon monoxide
(CO), nitrogren dioxide (NO_2), sulfur dioxide (SO_2),
20 hydrogen chloride (HCl), hydrogen fluoride (HF) and
hydrogen cyanide (HCN) are less than the maximium
specified in BSS 7239. The NBS smoke density
measurements using the definition of smoke in the
test of BSS 7238 and measuring optical density, D_s,
25 at 4 minutes is such that Ds is equal to or less than
about 500, preferably equal to or less than about 200
more preferably equal to or less than about 80 and
most preferably equal to or less than about 50.

The composition also exhibits reduced thermal
30 conductivity as measured by the procedure of Y.P.
Khanna, et al, _Polymer Engineering and Science_, vol.
16, p 1034 (1988) both before and after
carbonization. As used herein "carbonization" is a
process in which the resin system begins to form char
35 materials when exposed to a temperature of 1000°C
from a temperature of 25°C at a rate of 20°C/min in
an Argon atmosphere. (See Example 14) The thermal
conductivity before carbonization is general less

than about 60 w/mk, and after carbonization is from
less than about 60 to about 0.001 w/mk and the change
in conductivity on carbonization is equal to or less

5   than about 60 w/mk. In the preferred embodiments of
the invention, the thermal conductivity before
carbonization is equal to or less than 40 w/mk, after
carbonization is from less than about 40 to about
0.0001 w/mk and the change in thermal conductivity on

10 carbonization is equal to or less than about 40
w/mk. In the more preferred embodimentds of the
invention, the thermal conductivity before
carbonization is 30 w/mk, after carbonization is from
less than about 30 to about 0.001 w/mk and the change

15 in thermal conductivity on carbonization is less than
about 30 w/mk. In the most preferred embodiments of
the invention, the thermal conductivity before
carbonization is equal to or less than about 20 w/mk,
after carbonization is from less than about 20 to

20 about 0.01 w/mk and the change in thermal
conductivity on carbonization is less than about 20
w/mk.

The composition also maintains its mechanical
properties i.e. density and dimensions, to a

25 significant extent on carbonization. For example,
change in density and dimensions (thickness) is
preferably less than about 30%, preferably less than
about 20% and most preferably less than about 10%.

The fire retardant composition comprises two

30 essential ingredients. One of the essential
ingredients is a compoind which exhibits an
"endothermic effect" upon heating, or a mixture of
such compounds. As used herein, a compound which
exhibits an "endothermic effect" is whic absorbs heat

35 when exposed to fire or heat. Endothermic effect can
be measured by means of calorimetry. The net energy
absorbed can be expressed in term of joules per gram
of compound (J/gm). In general, the endothermic

effect greater than 0 J/gm. In the preferred
embodiments of the invention, the endothermic effect
of the compound is greater than about 1J/gm and in
5   the more preferred embodiemtns of the invention, the
endothermic effect is from about 1J/gm to about 1000
KJ/gm. In the most preferred embodiments of the
invention, the endothermic effect is from about
100J/gm to about 100KJ/gm.

10   In addition to the endothermic effect, it is
preferred that on heating or exposure to flame the
compounds produce inflammable gases such as
carbondioxide, steam, sulfur dioxide, nitrogen,
carbon monoixde, nitrous oxide, ammonia and the
15   like. A result is that the composition is converted
into a porous structure (containing pockets of gas)
preferably having a low heat thermal conductivity
(preferably below at about 30 w/mk, more preferably
from about 0.001 to about 20w/mk, and most preferably
20   from about 0.01 to 10 w/mk as measured by the method
of Khanna et al.).

Useful fire retardant agents may vary widely.
Illustrative of useful agents are such materials as
metal hydroxides and hydrated materials such as
25   magnesium hydroxide, calcium hydroxide, alumina
trihydrate, calcium nitrate hydrate, lithium
hydroxide monohydrate, and the like; carbonates and
bicarbonates such as potassium carbonate, magnesium
carbonate, calcium carbonate, potassium bicarbonate,
30   sodium bicarbonate, cadmium bicarbonate, cobalt
carbonate hydrate, erbium carbonate hydrate, europium
carbonate hydrate, lanthanum carbonate hydrate,
lithium carbonate and nickel carbonate hydroxide
tetrahydrate; metal nitrate hydratesfsuch as europium
35   nitrate hexahydrate neodymium nitrate hexahydrate,
cadmium nitrate tetrahydrate, calcium nitrate
hydrate, cobalt nitrate hydrate, cerium nitrate
hydrate, chromium nitrate hydrate, copper nitrate

hydrate, erbium nitrate pentahydrate; metal halide
hydrate, erbium nitrate pentahydrate; metal halide
hydrates as such erbium chloride hexahydrate,
europium chloride tetrahydrate, lanthanum chloride
5 heptahydrate, indium chloride hexahydrate, cadmium
bromide tetrahydrate, calcium chloride hydrate,
calcium chloride dihydrate, calcium bromide hydrate,
calcium iodide hydrate, cobalt chloride hexahydrate,
chromium chloride hexahydrate, and cobalt bromide
10 hydrate; metal sulfate hydrates such as europium
sulfate hydrate, indium sulfate hydrate, cerium
sulfate hydrate, cadium sulfate dihydrate, chromium
potasium sulfate dodecahydrate, chromium sulfate
hydrate, copper sulfate pentahydrate and erbium
15 sulfate hydrate; metal perchlorate hydrates such as
copper perchlorate hexahydrate, maganese perchlorate
hexahydrate, and sodium perchlorate monohydrate;
metal perborate hydrates such as sodium perborate
tetrahydrate and the like; metal sulfites and
20 bisufites such as potassium sulfite, sodium
bisulfite, sodium sulfite and the like; metal and
non-metal perchlorates such as ammonium perchlorate
and the like; metal and non-metal hydroxides such as
ammonium hydroxide and the like; and borates such as
25 zinc borate and the like; phosphate salts such as
sodium phosphate tribasic dodecahydrate, sodium
pyrophosphate decahydrate and the like; various
nitrogen containing organic compounds which thermally
decompose to form nitrogen gas such as
30 dinitrosopentamethylenetetramine (DNPT),
azodicarbonamide, p-toluenesulfonyl semicarbazide,
5-phenyltetrazole, diisopropylhydrazodicarboxylate,
p-toluenesulfonyl hydrazide, 4-4'-oxybis (benzene
sulfinyl hydrazide), 5-phenyl-3,6-dihydro-
35 1,3,4-oxadiazin-2-one, and hydroxyazoalkanes.
Preferred flame retardant agents are
metal hydroxides and hydrated materials, carbonates,
bicarbonates, nitrate hydrates, metal halide

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hydrates, sulfate hydrates, perchlorate hydrates,
phosphate hydrates, sulfites, bisulfites, borates,
perchlorates, hydroxides, phosphate salts, and
nitrogen containing compounds which thermally
decomposes to form nitrogen. More preferred flame
retardant agents are hydroxides, hydrates,
carbonates, bicarbonates, sulfites, and bisulfites.
Most preferred flame retardant agents are hydroxides,
carbonates, bicarbonates and hydrates, with hydrated
flame retardant agents being the agents of choice.

The judicious selection of fire retardants
depends on a number of factors which include their
efficiency and decomposition characteristics. Blends
of several types of fire retardants provide a viable
means to generate systems offering a wide spectrum of
thermal decomposition behavior and additional
beneficial chemical reactions. For example, a
mixture of magnesium nitrate and sodium carbonate
would react as follows.

1) $Mg(NO_3)_2 + Na_2CO_3 \longrightarrow MgCO_3 + 2NaNO_3$

2) $MgCO_3 \longrightarrow MgO + CO_2$
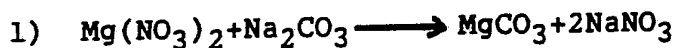
The incorporation of various types of catalysts,
promoters or the like can lower the thermal
decomposition temperature of the fire retardant or
mixture of retardants to increase the fire
retardant's efficiency.

In the prefered embodiments the fire retardant is
reusable after use. For example, when exposed to
fire, $Mg(OH)_2$ decomposes at about 320°C forming MgO
and water which is a fire retardant. Once the fire
is removed or extinguished, the MgO can be hydrated
with water to form magnesium hydroxide as follows:

$$\text{MgO} + \text{H}_2\text{O} \underset{320°C}{\overset{20°C}{\rightleftharpoons}} \text{Mg(OH)}_2$$
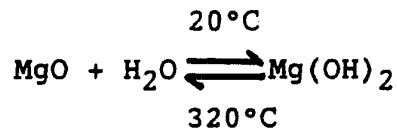
Furthermore, the various fire retardants can be recycled such that the mechanisum of fire retardance can be changed in the recycling. For example, magnesium carbonate decomposes on exposure to fire to form MgO and CO_2 gas. Afterwards, $Mg(OH)_2$ is formed on the reaction of the residual MgO with water. Thereafter, on exposure to a second fire, $Mg(OH)_2$ decomposes to form water in the gaseous and MgO.

The flame retardant agent is preferably in particulate form. Particle size may vary widely and is not critical. Usually flame retardant particle sizes are from about 0.001 microns to about 1000 microns. Preferred particle size are from about 0.01 to about 500 microns, more preferred particle sizes are from about 0.1 to about 100, and most preferred particle sizes are from about 0.1 to about 50 microns.

The flame retardant agent is preferably dispersed in a non-flammable polymeric matrix. As used herein, "non-flammable" means that the matrix material will not ignite when subjected to the Torch Test (See the Example). The type of polymer used to form the matrix may vary widely, the only requirement is that the material is non-flammable. In the preferred embodiments of the invention, the polymeric matrix material exhibits high temperature performance and high char yield. In the preferred embodiments of the invention, the matrix material and the fire retardant agent forms a reactive system. When it is subject to severe heating or exposed to flame, the fire retardant forms a gaseous by-product which converts the matrix material into a porous structure maintaining to a large degree its dimensions. This

porous structure exhibits sufficient mechanical
integrity, and a relatively low thermal conductivity
(less than 30 w/mk, preferably from about 0.001 to
about 20w/mk, more preferably from about 0.01 to
about 10 w/mk as determined by differential scanning
calorimetry (DSC) using the procedure of Y.P. Khanna,
et al, <u>Polymers Engineering and Science</u>, vol 16, p
1034 (1988)). The porous structure reduces the
transfer of heat to the underlying fibrous layer 12.

Useful polymers for forming the matrix include
those discussed above for formation of the matrix of
fibrous layer 12 which are non-flammable.
Illustrative of such non-flammable polymers are
thermoplastic polymers such as halopolymers as for
example poly(tetrafluoroethylene) and copolymers
thereof, and aromatic polyamides and polyesters such
as poly(metaphenylene isophthalamide)
poly(p-terephthalamide), poly (para-hydroxy benzoate)
and aromatic liquid crystalline polymers. Useful
non-flammable polymers also include thermosetting
resins such as unsaturated polyesters, phenolics,
epoxies, allylics, alkyds, aminoplastics, polyimides
and the like,, especially aromatic thermosets such
as, phenolics, aminoplastics, polyimides, and the
like.

Preferred matrix materials are thermosetting
resins and more preferred matrix materials are
aromatic themosetting resins. Most preferred
materials for use in the practice of this invention
are non-flammable in the Torch Test. These most
preferred materials also produce no or substantially
no smoke and toxic gases under BSS 7239 and BSS 7238
(an optional density or Ds at 4.0 minutes equal to or
less than about 500, preferably equal to or less than
about 200, more preferably equal to or less than
about 80 and most preferably equal to or less than
about 50 under BSS 7238, and toxic gases less than

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3500 ppm carbon monoxide, 100 ppm nitrogen dioxide,
100 sulfur dioxide, 500 ppm hydroge chloride, 200
hydrogen fluoride and 150 ppm hydrogen cyanide using
5   the procedure of BSS 7239). These preferred
compostions also exhibit reduced thermal
conductivities on carbonization (generally less than
about 30 w/mk, preferably less than about 20 w/mk,
more preferably from about 0.001 to about 20 w/mk,
10 and most preferably from about 0.01 to about 10 w/mk)
as measured by the procedure of Y.P. Khanna, et al,
Polymers Engineering and Science , vol 16, p 1034
(1988), and exhibit reduced changes in dimension
(i.e. density and thickness) on carbonization
15 (general less than about 30%, preferably less than
about 20%, more preferably less than about 10% and
most preferably less than about 5%).
     In the preferred embodiments of the invention,
the matrix material exhibits a net endothermic
20 effect; that is the material absorbs heat when
subjected to heat or a flame. The amount of heat
absorbed is greater than about 0J/gm as measured by
differential scanning salorimetry (DSC). In the
preferred embodiments of the invention, the net
25 endothermic effect is greater than about 1J/gm, and
in the more preferred embodiments of the invention
the net endothermic effect is from about 1J/gm to
about 1000KJ/gm. In the most preferred embodiments
of the invention, the net endothermic effect is from
30 about 100 J/gm to about 100KJ/gm.
     The nature of the net endothermic effect may vary
widely. For example, the effect may arise from
carbonization reactions, endothermic decomposition
reactions, curing reactions, combinations of the
35 foregoing reactions and the like. In the most
preferred embodiments of the invention where the
matrix material is a partially cured or completely
cured thermoset material, the endothermic effect

arises predominantly from carbonization and curing of
the matrix material. In these embodiments, the
matrix material is selected from the group consisting
of partially cured thermosetting resins i.e. those in
which less than about 100% of curable groups are
cured as shown by the procedure of J.F. Rabek,
"Experimental Methods in Polymer Chemistry", Wiley
and Sons, New York, New York, (1980). The degree of
curing will vary widely depending on a number of
factors such as the consistency of the material. In
general, the degree of cure is equal to or less than
about 0.5. In the preferred embodiments of the
inventions, the degree of cure is from about 0.15 to
about 0.50 and in the more preferred embodiments of
the invention the degree of cure is from about 0.25
to about 0.50. In these embodiments of the invention
the degree of cure is from about 0.30 to about 0.50
with those embodiments in which the degree of cure is
from about 0.40 to about 0.50 being the embodiments
of choice. In these embodiments of the invention,
the partially cured resin further cures on subjection
to heat and/or flame absorbing heat and decreasing
the amount of heat transmitted to fibrous layer 12.
The further cured resin which is formed is usually
more resistance to the transmission of heat than the
partially cure material which further enhances the
effectiveness of layer 14. Illustrative of such most
preferred matrix materials are those which are formed
by cyclotrimerization of aromatic polycyanates, most
preferably those containing phenolic resins of the
type described in U.S. Patent Nos. 4,002,755,
4,831,086, and 3,444,137; WO871443; and PCT
87/001236. These resins can be used continuously at
relatively high temperatures most preferably higher
than about 500°F. The high temperature performance
arises from two sources, the inherently high aromatic
content of the phenolic resin and the triazine ring

structure resulting from trimerization of cyanate
groups. unlike other high temperature resins, these
resins are easily processable using conventional
5   equipment.
These phenolic cyanate resins are generally of the
following Formula I:

<u>Formula I</u>

10

15
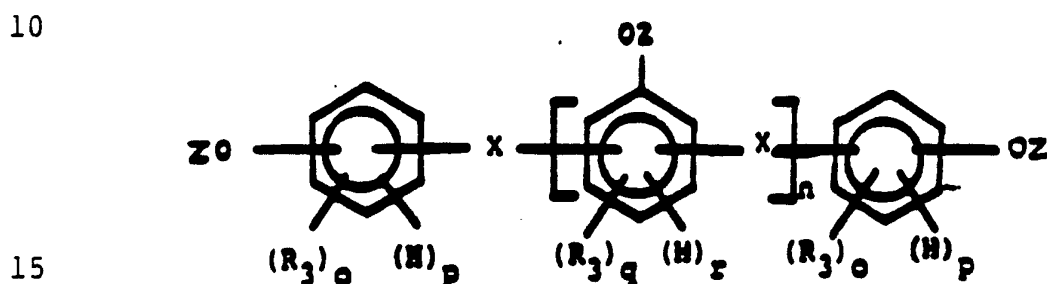
wherein:

n is a positive whole number greater than or
equal to 1;

20   q and r are the same or different at each
occurence and are whole numbers from 0 to 3, with the
proviso that the sum of q and r at each occurrence is
equal to 3;

Z is -CN, hydrogen and -CN;

25   o and p are the same or different at each
occurrence and are whole numbers from 0 to 4 with the
proviso that the sum of o to p at each occurrence is
equal to 4;

-X- is a divalent organic radical; and

30   R_3 is the same or different at each occurrence
and is a substituent other than hydrogen.

In the structure of Formula I, R_3 is a
substituent other than hydrogen. Illustrative of
suitable R_3 groups are such substituents as halogen,
35   trihalomethyl, cyano, alkyl, alkoxy, phenyl alkynyl,
isocyanate, and the like.

Illustrative of suitable -X- groups are alkylene
such as methylene, ethylmethylene,

2-ethylpentylmethylene, methylmethylene,
isopropylmethylene, isobutylmethylene,
pentylmethylene, and furylmethylene, and the like;
arylenes such as 1, 3-benzenedimethylene,
phenylmethylene, 1,4-benzendimethylene,
2,2-bis-(4-phenylene) propane,
4-methoxyphenylmethylene, bis-(4-phenylenemethane),
4,4-diphenylene dimethylethane; and cycloalkylenes
such as cyclohexylene, cyclooctylene, and
1,3-cyclohexane-dimethylene, and the like.

Preferred are those embodiments of Formula I in
which:

Z is -CN, or hydrogen and -CN, preferably when Z
is hydrogen and -CN from about 5 to about 100 mole
percent of the Z moieties are -CN;

-X- is 1,4-phenyldimethylene substituted or
unsubstituted methylene wherein permissible
substituents are alkyl, benzene, halogen, or furyl
-O-,-SO$_2$-,-S-,-S-S-,-C(O)-,-OC(O)- or -C(O)O-

q and r are the same or different at each
occurrence and are positive whole numbers from 0 to
3, with the proviso that the sum of q and r is 3;

R$_3$ is alkyl;

n is a positive integer from 1 to about 10; and

o and p are the same or different at each
occurrence and are positive integer from 0 to 4, with
the proviso that the sum of o and p is 4.

Amongst the preferred embodiments, particularly
preferred are those embodiments of above Formula I in
which:

Z is hydrogen, or hydrogen and -CN with the
proviso that from about 20 to about 100 mole percent
of Z moieties are -CN;

-X- is methylene, methylene substituted with
alkyl having from about 1 to about 10 carbon atoms,
benzene, halogen or furfuryl, or xylene;

R_3 is methyl or ethyl;

o is 0 or 1;

p is 0 or 1;

5   n is 1 to about 8, and more preferably 1 to 6;

q is 0 or 1

r is 1 to 3; and

p is 1 to 4.

Other preferred embodiments are those embodiments of

10 the Formula I wherein:

n is 1 to about 5;

Z is -CN or hydrogen and -CN with the proviso

that from about 60 to about 100 mole percent Z

moieties are CN;

15   q is 0;

o is 0; and

X is methylene, methylene substituted with one or

more alkyl of 1 to 10 carbon atoms, halogen, benzene

or furfuryl or xylene,

20 r is 3; and

p is 4.

The amount of fire retardant agent loaded into

the matrix may vary widely. In general, the greater

the amount of agent and the greater the amount of

25 inflammable gas produced per mole of agent the higher

the degree of fire retardance. Conversely, the lower

the amount of agent and the lower the amount of

gasous decomposition products produced by the agents

per more the lower the degree of fire retardance. In

30 general, the amount of agent is at least about 1

weight percent based on the total weight of the fire

retardant layer. In the preferred embodiments of the

invention, the amount of agent is from about 1 to

about 99 weight percent based on the total weight of

35 the fire retardant layer, and in the particularly

preferred embodiments of the invention, the amount of

agent is from about 5 to about 95 weight percent on

the aforementioned basis. In the most preferred

embodiments of the invention, the amount of agent is
from about 10 to about 90 weight percent based on the
total weight of the fire retardant layer.

5   Fire retardant layer 14 can be formed using
conventional techniques for formation of polymer
blends in multi-layers. Such polymer blending
techniques are known in the art and will not be
described herein in detail.

10   Each layer 14 may be composed of one or more
different polymers with one or more fire retardant
agents which decompose on heating to form one or more
inflammable gasous materials. The selection of
specific components of layer 14 and construction of

15 layer 14 depends on application. The efficiency and
decomposition behavior of layer 14 can be tailored to
suit a specific application by proper selection of
polymer and fire retardant and by addition of a
catalyst or promoters. For example, sodium

20 bicarbonate decomposes between 100°C to 140°C with
the evolution of CO_2 and H_2O, forming sodium
carbonate. The theoretial gas yield is 267 CM^3/gm,
but thermal decomposition normally yields only about
135 cm^3/gm. At a temperature of 140°C, decomposition

25 becomes more rapid. The rapid diffusion of CO_2 makes
the production of a stable closed cells extremely
difficult. The addition of an equivalent amount of
acid to the sodium bicarbonate increases the gas
yield.

30   The shape of fire retardant layer 14 and the area
percent of fibrous layer 12 bonded to fire retardant
layer 14 may vary widely. For example, fire
retardant layer 14 may be in the form of a sheet or
sheet-like (e.g. contiguous or overlapping ribbons,

35 steps, squares and the like which form a sheet-like
layer) which is bonded to or in contract with 100
percent or substantially one hundred percent of a
surface of fibrous layer 12. Alternatively, layer

may be formed from a plurality of various
geometrically shaped polymeric bodies (e.g. ribbons,
hexagons, triangles, rectangles, squares, strips)

5   which cover less than 100% of the surface of fibrous
layer 12. In the preferred embodiments of this
invention, fire retardant layer 14 is formed from
sheets, strips, ribbons and the like and is bonded to
a least about 5 area percent of a major surface of

10 fibrous layer 12. In the more preferred embodiments
of the invention, fire retardant layer 14 is bonded
to at least about 20 area percent of a major surface
of fibrous layer 12, and in the most preferred
embodiments of the invention, fire retardant layer 14

15 is bonded to at least about 50 area percent of a
major surface of fibrous layer 12. In the
embodiments of choice, fire retardant layer 14 covers
at least 95 area percent of a major surface of
fibrous layer 12.

20   While not an essential component, fire retardant
layer 14 may itself comprise a network of fibers as
described for use in the fabrication of fibrous layer
12 dispersed in the polymeric matrix. Fibers for
inclusion in fire retardant layer 14 are preferably

25 formed from non-flammable materials. As used herein,
"non-flammable" means material is not ignited when
exposed to flame in the Torch Test. Such materials
include non-flammable metallic materials,
semi-metallic materials, non-metals materials and

30 organic materials. Illustrative of useful and
preferred inorganic fibers are S-glass fibers, S_2
glass fibers, silicon carbide fibers, asbestos
fibers, basalt fibers, E-glass fibers, alumina
fibers, alumina-silicate fibers, quartz fibers,

35 zirconia-silica fibers, boron fibers, carbon fibers,
graphite fibers, non-alkaline aluminoborosilicate
fibers, soda borosilicate fibers, soda silicate
fibers, soda lime-aluminosilicate fibers, lead

silicate fibers, non-alkaline lead boroalumina
fibers, non-alkaline barium boroalumina fibers,
non-alkaline zinc boroalumina fibers, non-alkaline
iron fibers, cadmium borate fibers and the like.
Exemplary of useful metallic or semi-metallic fibers
are those composed of boron, aluminum, steel and
titanium.

Illustrative of useful organic filaments are
those composed of highly aromatic thermosetting and
thermoplastic polymers such as for example,
poly(metaphenylene isophtahalamide) (Nomex®),
poly(p-phenylene terephtahalamide) (Kevlar®) and
liquid crystalline polymers such as liquid crystal
copolyesters, aromatic polyamides, and the like.

Preferred fibers are aramid fibers, liquid
crystal polyester fibers and glass fibers such as
E-glass and S-glass. Suitable aramid fibers formed
principally from aromatic polyamide are described in
USP 3,671,542, which is hereby incorporated by
reference. Preferred aramid filament will have a
tenacity of at least about 20 g/d, a tensile modulus
of at least about 400 g/d and an energy-to-break at
least about 8 joules/gram, and particularly preferred
aramid fibers will have a tenacity of at least about
20 g/d, a modulus of at least about 480 g/d and an
energy-to-break of at least about 20 joules/gram.
Most preferred aramid fibers will have a tenacity of
at least about 20 g/denier, a modulus of at least
about 900 g/denier and an energy-to-break of at least
about 30 joules/gram. For example, poly(phenylene
terephthalamide) fibers produced commercially by
Dupont Corporation under the trade name of Kevlar®
29, 49, 129 and 149 having moderately high moduli and
tenacity values are particularly useful in forming
ballistic resistant composites. Also useful in the
practice of this invention is poly(metaphenylene
isophathalamide) fibers produced commercially by

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Dupont under the tradename Nomex®.

Suitable liquid crystal copolyesters, fibers are
disclosed, for example, in U.S. Patents 3,975,487;
4,118,372; and 4,161,470, hereby incorporated by
reference. Tenacities of about 15 to 30 g/d and
preferably about 20 to 25 g/d, and modulus of about
500 to 1500 g/d and preferably about 1000 to 1200
g/d, are particularly desirable.

Most preferred fibers are formed from inorganic
materials. Of these, glass fibers are the fibers of
choice.

In these embodiments of the invention, in which
fire retardant layer 14 includes fibers, the fibers
are dispersed in a continuous phase of matrix
material which preferably substantially coats each
filament contained in the bundle of filament. The
manner in which the fibers are dispersed may vary
widely. The fibers may be aligned in a substantially
parallel, unidirectional fashion, or fibers may be
aligned in a multidirectional fashion with filaments
at varying angles with each other. In the preferred
embodiments of this invention, fibers in each fire
retardant layer 14 are aligned in a substantially
parallel, unidirectional fashion such as in a
prepreg, pultruded sheet and the like. One such
suitable arrangement is where fire retardant layer 14
comprises a plurality of layers or laminates in which
the coated fibers are arranged in a sheet-like array
and aligned parallel to one another along a common
fiber direction. Successive layers of such coated,
uni-directional fibers can be roated with respect to
the previous layer. An example of such laminate fire
retardant layer 14 are composites with the second,
third, fourth and fifth layers roated +45°, -45°, 90°
and 0°, with respect to the first layer, buy not
necessarily in that order. Other examples include
composites with 0°/90° layout of yarn or filaments.

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Articles 10 of this invention can be fabricated using a number of procedures. For example, the layers are formed by molding the combination of
5 layers and fibrous layers in the desired configurations and amounts by subjecting the combination to heat, and pressure during a mold cycle time. The molding temperature is critical and is usually selected such that it is less than the
10 melting or softening point of the polymer from which the fibers of fibrous layer 12 and/or fire retardant layer 14 are formed of or the temperature at which fiber damage occurs, but is greater than the melting point or softening point of the polymer or polymers
15 forming the polymeric layer(s). For example, for extended chain polyethylene filaments, molding temperatures range from about 20 to about 150°C, preferably from about 80 to about 145°C, more preferably from about 100 to about 135°C. The
20 molding pressure may vary widely and preferably may range from about 10 psi (69 kPa) to about 10,000 psi (69,000 kPa). A pressure between about 10 psi (69 kPa) and about 100 psi (690 kPa), when combined with temperatures below about 100°C for a period of time
25 less than about 1.0 min., may be used simply to cause the fibrous layers and polymeric layers to stick together. Pressures from about 100 psi to about 10,000 psi (69,000 kPa), when coupled with temperatures in the range of about 100 to about 155°C
30 for a time of between about 1 to about 5 min., may cause the filaments of the fibrous layers to deform and to compress together (generally in a film-like shape). Pressures from about 100 psi (690 kPa) to about 10,000 psi (69,000 kPa), when coupled with
35 temperatures in the range of about 150 to about 155°C for a time of between 1 to about 5 min., may cause the film to become translucent or transparent. For polypropylene filaments, the upper limitation of the

temperature range is preferably about 10 to about
20°C higher than for ECPE filament and for aramid
fibers, the upper limitation of the temperature range
5   is preferably about 20°C to about 30°C higher than
for ECPE fibers.

Fibrous layer 12 may be bonded to fire retardant
layer 14 by any suitable bonding means known to those
of skill in the art. Illustrative of useful
10   attaching mans are adhesive such as those described
in Liable, Chapter 6, supra, bolts, screws,
mechanical interlocks adhesives such as metal and
non-metal adhesives, organic adhesives and the like.
In the preferred embodiments of this invention,
15   attaching means is selected from the group consisting
of adhesive bonding agents formed the matrix material
forming layers 12 and 14.

The number of layers 12 and 14 included in
article 10 of this invention may vary widely
20   depending on the uses of the article, for example, in
those uses where the would be used as ballistic
protection desired and other factors known to those
of skill in the ballastic protection are. In general
for this application, the greater the degree of
25   protection desired the greater the number of layers
included in the article for a given weight of the
article. Conversely, the lessor the degree of
ballistic protection required, the lessor the number
of layers required for a given weight of the article.
30   FIG. 2 shows a variant of the embodiment of FIG.
1 which is indicated at 16. Article 16, comprises a
fibrous layer 18 bonded on one side by fire retardant
layer 20 and bonded on the other side by fire
retardant layer 22. Fibrous layer 18 is as described
35   herein above for fibrous layer 12 of the embodiment
of FIG. 1. Fire retardant layers 20 and 22 can be
fabricated from the same or different materials and
are as described herein above for fire retardant

layer 14 of the embodiment of FIG. 1.

FIG. 3 depicts an armor article 24 which differs from article 16 of FIG. 2 by the inclusion of a hard
5   impact layer 26, corresponding parts being referred to by like numerals. Layer 26 is formed from a plurality of planar bodies 28 composed of a hard material having a hardness of at least about a Brinnell hardness of 25 or a Mohs hardness of 2 and
10 functions to shatter, blunt or crack the impacting projectile.. Useful materials for the farbicationn of layer 26 may vary widely and include materials normally used in the fabrication of ballistic resistant armor which function to partially deform
15 the initial impact surface of a projectile or cause theprojectile to shatter. Such materials include metals such as steel, titanium, aluminum and the like and non-metal ceramic materials such as those described in C.F. Liable, Ballistic Materials and
20 Penetration Mechanics, Chapters 5-7 (1980) and include single oxides such as aluminum oxide (Al_2O_3), barium oxide (BaO), beryllium oxide (BeO), calcium oxide (CaO), cerium oxide (Ce_2O_3 and CeO_2), chromium oxide (Cr_2O_3), dysprosium oxide (Dy_2O_3), erbium oxide
25 (Er_2O^3), europium oxide: (EuO, Eu_2O_3, and Eu_2O_4), ($Eu_{16}O_{21}$), gadolinium oxide (Gd_2O_3), hafnium oxide (HfO_2), holmium oxide (Ho_2O_3), lanthanum oxide (La_2O_3), lutetium oxide (Lu_2O_3), magnesium oxide (MgO), neodymium oxide (Nd_2O_3), niobium oxide: (NbO,
30 Nb_2O_3), (Nb_2O_5), plutonium oxide: (PuO, Pu_2O_3, and PuO_2), praseodymium oxide: (PrO_2, Pr_6O_{11}, and Pr_2O_3), promethium oxide (Pm_2O_3), samarium oxide (SmO and Sm_2O_3), scandium oxide (Sc_2O_3), silicon dioxide (SiO_2O, strontium oxide (StO), tantalum oxide
35 (Ta_2O_5), terbium oxide (Tb_2O_3 and Tb_4O_7), thorium oxide (ThO_2), thulium oxide (Tm_2O_3), titanium oxice: (TiO, Ti_2O_3, Ti_3O_5 and TiO_2), uranium oxide (UO_2, U_3O_8 and UO_3), vanadium oxide (Vo, V_2O_3, VO_2 and

V_2O_5), ytterbium oxide (Yb_2O_3), yttrium oxide (Y_2O_3),
and zirconium oxide (ZrO_2). Useful ceramic materials
also include boron carbide, aluminum beride, aluminum

5 carbide, boron carbide, silicon carbide, aluminum
carbide, titanium nitride, boron nitride, titanium
carbide, titanium diboride, iron carbide, iron
nitride, barium titanate, aluminum nitride, titanium
niobate, boron carbide, silicon boride, barium

10 titanate, silicon nitride, calcium titanate, tantalum
carbide, graphites, tungsten; the ceramic alloys
which include cordierite/MAS, lead zirconate
titanate/PLZT, alumina-titanium carbide,
alumina-zirconia, zirconia-cordierite/ZrMAS; the

15 fiber reinforced ceramics and ceramic alloys; glassy
ceramics; as well as other useful materials.
Preferred are non-metal and metal ceramic materials.
Preferred ceramic materials are aluminum oxide, and
metal and non-metal nitrides, borides and carbides.

20   FIG. 4 depicts a ballistic resistant article 30
which differs from article 16 of FIG 2 by the
inclusions of layers 32,34, 36 and 38 corresponding
parts being referred to by like numbers. Surface
layers 32 and 36 coat article 30 and function as the

25 initial barrier to heat and flame. Layers 32 and 36
are preferably formed of a refractory material as for
example ceramic materials used to form impact layer
26 of article 24. Such materials are generally
applied to form layers 32 and 36 in the form of

30 refactory ceramic paints, as for example Fiberfrax®
coating cement made by Carborundum, Inc. Such paints
or coatings are usually comprised of a refractory
ceramic material dispersed in a liquid vehicle
comprised of a liquid and a polymeric binder. In the

35 preferred embodiments of the invention, the various
components of the paint or coating are selected such
that the paint or coating forms or expands on heating
decreasing the thermal conductivity of the coating to

levels preferably less than about 30w/mk, more
preferably less than about 20 w/mk and most
preferably less than about 10 w/mk. Layers 20 and 22

5   are the same or different and are as described above
in the description of article 16 of FIG 2. In the
embodiment of FIG 4, layers 20 and 22 are preferably
formed of a fire retardant composition comprised of a
particulate material such as $Mg(OH)_2$ which produces a

10 non-flammable gas when heated or exposed to flame in
a resin matrix preferably a partially cured
thermosetting resin, such are the phenolic cyanate
resin described in U.S. Patent No. 4,831,086.

     Layer 18 is a described above and consists of a .

15 ballistically effective fiber filled polymeric
composite such as a polymeric matrix consist of a
mixture of a thermosetting resin as for example a
vinyl ester resin and a thermoplastic resin such as a
polyurethane filled with a flammable fiber such as

20 extended chain polyethylene fibers as for example,
Spectra® 900 and Spectra® 1000 polyethylene fibers or
with an inflammable fiber which generates smoke and
toxic gases when exposed to heat and/or flame such as
aramid fibers as for example Kevlar® 29, 49, 129 or

25 149 aramid fibers or fibers formed from polyimides
and halogenated materials such as polyvinyl chloride.

     Outer surface protective layers 34 and 38 are the
same or different and are formed from materials
selected from the group consisting of permissible

30 materials for the fabrication of Layer 14 of FIG 1,
and of Layers 20 and 22 of FIGS 2 to 4. In the
preferred embodiments of the invention, layers 34 and
38 function to protect layers 20 and 22 from heat and
flame for time sufficient to allow the partially

35 cured matrix material of layers 20 and 22 to further
cure so that layers 20 and 22 can achieve enhance
high temperature resistance. Layers 34 and 38 are
preferably formed from a fire retardant composition

comprised of resin matrix material which generates
little or no visible smoke when exposed to heat
and/or flame as for example those which do not
contain aromatic groups, halogens or unsaturations
such as polyvinyl acetate, polyacetal, polyethylene,
polypropylene and the like, filled with a particulate
inorganic material which forms a non-flammable gas
when exposed to heat and/or flame such as a metal
hydroxide or hydrate such as $Mg(OH)_2$.

The relative volume percents of the various
layers 18, 20, 22, 32, 34, 36, and 38 may vary
widely. In general, layer 18 will comprise at least
about 50 volume percent based on the total volume of
article 30 and produces the bulk of the ballistic
protection. Layer 18 preferably comprise at least
about 60 volume percent, more preferably at least
about 80 volume percent and most preferably at least
about 90 volume percent of article 10 based on the
total volume of the article.

Of the volume of article 30 formed by layers 20,
22, 32, 34, 36 and 38, layers 20 and 22 generally
form at least about 50 volume percent, preferably at
least about 60 volume percent, more preferably at
least about 80 volume percent and most preferably at
least about 90 volume percent based on the total
volume of layers 20, 22, 32, 34, 36 and 38. Those
embodiments in which layers 20 and 22 constitute at
least about 95 volume percent of the volume of
article 30 exclusive of layer 18 are the embodiments
of choice.

The article of this invention can be used for
conventional purposes. For example, such composites
can be used in the fabrication of penetration
resistance articles ballistic armor, spall liners,
structural parts and the like using conventional
methods.

The following examples are presented to provide a

more complete understanding of the invention and are
not to be construed as limitations thereon.

EXAMPLE 1

One side of 1" (2.54 cm) thick Spectra® panel was
laminated with two layers of glass fabric prepreg.
The outside layer, which was 0.0417 inch (0.106 cm)
thick, was impregnated with a magnesium hydroxide
filled poly(vinylacetate emulsion). The weight ratio
of filler/resin solid was 2:1). The inside glass
layer, which was 0.0833 inch (0.212 cm) thick was
impregnated with a magnesium hydroxide filled
phenolic cyanate resin (filler/resin solid was 2:1).
A K-type thermocouple was placed at the center of
the panel between the Spectra® panel and the glass
layer for temperature measurement. The composite
panel was molded at 125°C for 2 hours at 1 ton (906
Kg) press pressure. The glass side of the panel was
painted with a layer of a refractory ceramic coating.
The glass side of the panel was exposed to a
propane torch for ten minutes. Neither visible smoke
nor burning flame was observed during the entire
experiment. The temperature at the interface between
glass layer and Spectra® panel was found to be 185°C
after 3 minutes and below 265°C during the entire 10
minutes experiment.

COMPARATIVE EXAMPLE 1

The procedure of Example 1 was followed with
the exception that the glass fabric prepreg was
impregnated with resin without magnesuim hydroxide.
The glass side of the panel was exposed to a propane
torch. Smoke and flame of burning were observed
during the first 10 seconds of the burning. No
further smoke or fire was observed during the
remainder of the experiment. The temperature at the
interface between glass layer and Spectra® panel was

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found to be 400°C after only 3 minutes of burning and
the temperature increased rapidly thereafter. No
further temperature measurement was made because the
thermocouple was detacked due to severe delamination
of the composite.

                         EXAMPLE 2

        The procedure of Example 1 was followed with
the exception that the refractory ceramic coating was
not applied. The temperature at the interface
between the glass layer and Spectra® panel was found
to be 191°C after 3 minutes and below 215°C during
the first six minutes of the experiment. No further
temperature measurement was made because the
composite was delaminated. Neither visible smoke nor
burning flame was observed during the entire
experiment.

                         EXAMPLE 3

        The formulation/composition, manufacturing
procedure, and test method of Example 1 were employed
except that the inside glass layer was impregnated
with a magnesium hydroxide filled vinyl ester resin.
The resin was a mixture of Derakane® 8087 (Dow
Chemical) containing 1% Luposal peroxide (Lucidal
chemcial) as the curing agent. The weight ratio of
filler/resin solids was 2:1. A K-thermocouple was
placed at the center of the panel between the
Spectra® panel and the glass layer for temperature
measurement. The composite panel was molded at 125°C
for 2 hours at 1 ton (906 Kg) press pressure.

        The glass side of the panel was exposed to a
propane torch for ten minutes. The temperature at
the interface between glass layer and Spectra® panel
was found to be 245°C after 3 minutes. No further
temperature measurements were made, because the
thermocouple was detached due to severe delamination
of the composite. Very little visible smoke and no

burning flame was observed during the entire
experiment.

EXAMPLE 4

The formulation/composition, manufacturing
procedure, and test method of Example 2 were
followed, except that the inside glass layer was
impregnated with a magnesium hydroxide filled epoxy
resin. The resin was a mixture of DER 331® and 26
pph of methylene dianiline (Aldrich Chemical) as the
curing agent. The weight ratio of filler to resin
solids was 2:1. A K-type thermocouple was placed at
the center of the composite between the Spectra®
panel and the glass layer for temperature
measurement. The composite panel was molded at 125°C
for 2 hours at 1 ton (906 Kg) press pressure.

The glass side of the panel was exposed to a
propane torch for ten minutes. The temperature at
the interface between glass layer and Spectra® panel
was found to be 285°C after 3 minutes. No further
temperature measurement were made because the
thermocouple was detached due to severe delamination
of the composite. Visible smoke but no burning flame
was observed during the experiment.

EXAMPLE 5

The formulation/composition, manufacturing
procedure, and test method of Example 2 were
employed, except that the inside glass layer was
impregnated with a magnesium hydroxide filled one
step phenolic resole clear resin (Schenectady
Chemicals). The weight ratio of filler to resin
solids was 2:1. A K-type thermocouple was placed at
the center of the panel between the Spectra® panel
and the glass layer for temperature measurement. The
composite panel was molded at 125°C for 2 hours at 1
ton (906 Kg) press pressure.

The glass side of the panel was exposed to a
propane torch for ten minutes. The temperature at
the interface between glass layer and Spectra® panel
5   was found to be 250°C after 1 minute. No further
temperature measurements were made because the
thermocouple was detached due to severe delamination
of the composite. Little visible smoke but no
burning flame was observed during the experiment.

10

EXAMPLE 6

The formulation/composition, manufacturing
procedure, and test method of Example 1 was followed,
except that the inside glass layer was impregnated
15 with a magnesium hydroxide filled PMR-15 polyimide
resin (Dexter Composites). The weight ratio of
filler to resin solids was 2:1. A K-type
thermocouple was placed at the panel between the
Spectral® panel and the glass layer for temperature
20 measurement. The composite panel was molded at 125°C
for 2 hours at 1 ton (906 Kg) press pressure.

The glass side of the panel was exposed to a
propane torch for ten minutes. The temperature at
the interface between glass layer and Spectra® panel
25 was found to be 320°C after 2 minutes. No further
temperature measurements were made because the
thermocouple was detached due to severe delamination
of the composite. Little visible but no smoke
burning flame was observed during the experiment.

30

EXAMPLE 7

Using the composite of Example 1, experiments
were carried out to measure the smoke intensity using
the Hot Metal Balls (spall) Contact Test. The spall
35 materials used were 1/2 lbs (0.227 kg) of 1/4" (0.635
cm) diameter copper balls and 2 lbs (0.908 kg) of 1"
(2.54 cm) diameter aluminum balls which were
purchased from Specialty Products International

(Keene, NH). Table 1 gives the description of the spall materials used.

5

Table 1: Simulated Spall Materials

Material	Diameter in(cm)	Type	Grade	Purity
Copper Ball	1/4 (0.635)	101	200	99.9%
Aluminum Ball	1 (2.54)	2017 T4	200	------

10

In the test, the test panel was positioned horizontally in a NBS smoke chamber prior to the onset of testing. On its surface, a 4 in(10.16 cm) inside diameter and 8 in(20.32 cm) outside diameter annular fixture was placed to serve as a guide for dropping the hot metal balls on to the designated areas. Separately, the 1/2 lb (0.227 kg) of copper balls were heated to 560°C and the 2 lbs (0.908 kg) of the aluminum balls were heated to 360°C by a gas burner.

In the test, the aluminum balls were first dropped on the 8in (20.32 cm) outside diameter areas and the copper balls were dropped on the 4in (10.16 cm) diameter areas. The chamber door was immediately closed and the smoke and toxic gas generated from the test panels were recorded.

The calculated surface temperature of the metal balls for both tests is given in Table 2.

35

Table 2: Surface Temperature of the Metal Balls
on the Sample Surface, Spectra® Panel °C

	Metal Temperature of the Sample, °C		Calculated
	Required	Initial	
Copper Balls	500.0	560.0	516.0
Aluminum Balls	300.0	360.0	314.0

The NBS smoke density measurement, as described
in Boeing test specification BSS 7238, is used to
evaluate the amount smoke generated during the hot
spall contact test.   This test is the standard test
for materials used in the interiors of civil
aircraft. The results of the test are given in Table
3.

In Table 3, the abbreviations have the following
meanings:

(1) Ds (Specific optical density)$= \frac{V}{LA} \log_{10} \frac{100}{T}$

where V is the chamber volume;

L is Light path length;

A is the exposed specimen area; and

T is % light transmission;

(2) Dm is the maximum specific optical
density whose value is calculated using the minimum
light transmittance observed during the test; and

(3) Dm (corr) is Dm-Dc, where Dc is the
specfic optical density corresponding to the "clean
beam" reading, TC, observed at the end of the test.

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Table 3

Smoke Generation from Spectra® Composite
During Hot Spall Contact Test

Properties	Value
% Transmittance (min)	46
Dm (corrected)	45
Time to Dm (mins)	5.0
Ds @ 1.5 minutes	42
Ds @ 4.0 minutes	45
Ds @ 16 minutes	0.18

Boeing Specification BSS 7238 of Ds @ 4
minutes ranges from 50 - 200. As indicated in Table
3, the composite of Example 1 does not release smoke
under the hot spall contact test.

EXAMPLE 8

Using the NBS chamber of Example 6 and the
procedure of Boeing Specification BSS 7239, the amount
of toxic gases evolved by the composite of Example 1
during the hot spall contact test was evaluated. Gas
emitted during the test are collected and the toxic
gas fraction is determined through analysis following
the procedure described in BSS 7239. The test results
are set forth in Table 4.

Table 4
Toxic Gases Emission from
Composite During Hot Spall contact

Gas	BSS 7239 (ppm)	Test Results (ppm)
Carbon Monoxide (CO)	3500	18
Nitrogen Dioxide (NO_2)	100	0
Sulfur Dioxide (SO_2)	100	0
Hydrogen Chloride (HCl)	500	0
Hydrogen Fluoride (HF)	200	0
Hydrogen Cyanide (HCN)	150	0

As seen from Table 4, the only toxic gas emitted
from the composite during the hot spall contact test

was carbon monoxide, and its concentration was very
low compared to the Boeing Specification.

5   EXAMPLE 9

Using the NBS chamber and procedure of Boeing
Specification BSS 7238 of Example 7, the smoke
generated from the composite of Example 2 is given in
Table 5.

10
                              Table 5

Smoke Generation from Spectra® Composite (Example 2)
During Hot Spall Contact Test

15   _____

     Properties   Value

     _____

     % Transmittance (min)   100
20   Dm(corrected)   0
     Time to Dm (mins)   20
     Ds @ 1.5 minutes

                                                      0

     Ds @ 4.0 minutes[4]   0
25   Dx = 16 (minutes)   --

     _____

As seen from this Example, the composite of
Example 2 without the ceramic refractory coating,
30 generated much less smoke than the composite of
Example 1 with a ceramic refractory coating.

                             EXAMPLE 10

Using the NBS chamber of Example 6 and the
35 procedure of Boeing Specification BSS 7239, the
amount of toxic gases evolved during the hot spall
contact test for the composite of Example 2 was
evaluated. Gases emitted during the test are

collected and the toxic gas fraction is determined
through analysis following the procedure described in
BSS 7239. The test results are set forth in the
5   following Table 6.

Table 6
Toxic Gases Emission from
Composite During Hot Spall contact

10

Gas	BSS 7239 (ppm)	Test Results (ppm)
Carbon Monoxide (CO)	3500	4
Nitrogen Dioxide (NO$_2$)	100	0
Sulfur Dioxide (SO$_2$)	100	0
Hydrogen Chloride (HCl)	500	0
Hydrogen Fluoride (HF)	200	0
Hydrogen Cyanide (HCN)	150	0

As seen from Table 6, the only toxic gas emitted
from the composite during the hot spall contact test
was carbon monoxide, and its concentration was very
25 low compared to the Boeing Specification, and was
even lower compared to Example 8.

EXAMPLE 11

In order to understand the temperature use
30 behavior of various systems described in Examples 1
to 10, experiments were performed to evaluate the
heat released (or exothermic heat expressed as a
"negative" quantity) and heat absorbed (or
endothermic heat expressed as "positive" quantity) of
35 these systems at a temperature between 25°C to 1000°C
using differential scanning calorimetry (DSC). The
heat of the curing reaction and the heat of
decomposition/carbonization reaction are the two

major sources of heat observed in this temperature
range. The term, "carbonization", is defined as a
process in which the resin system begins to form char
5   materials when heated from a temperature of 25°C to a
temperature of 1000°C at a rate of 20°C/min under an
Argon atmosphere as described in more detail in
Example 14 below. During this procedure, char begins
to form at some temperature which varies depending on
10   the resin material.

A DuPont Thermal Analyzer equipped with a DuPont
900 DSC cell was used. The scanning rate used was
20°C/Min in Argon. The sample size ranged from 5 to
12 mg. The results are set forth in the following
15   Table 7.

TABLE 7

Heat (J/gm)	Experimental			
	PT[1]	VE[2]	EP[3]	PH[4]
Curing Reaction	-437.3	-345.3	-323.3	-452.0
Decomposition/ Carbonization	-59.2	+313.4	-54.6	-186.2

25   1. "PT" is phenolic cycanate resin of Example 1 and 2.
2. "VE" is the vinyl ester resin of Example 3.
3. "EP" is the epoxy resin of Example 4.
4. "PH" is the phenolic resin of Example 5.

EXAMPLE 12

Following the procedure of Example 11, the
30   effect of the matrix on the thermal decomposition
behavior of the fire retardant system was evaluated.
The filler was magnesium hydroxide and the resins
were phenolic cyanate (PT), vinyl ester (VE), epoxy
resin (EP), phenolic resin (PH) and polyimide
35   (PMR-15). The weight ratio of resin to filler was 2
to 1. The results are set forth in the following
Table 8.

The Effect of Matrix on Heat Generation/Absorption
Behaviour of the Matrix/Mg(OH)$_2$ System(1:2)

TABLE 8

Heat (J/gm)	Experimental Results				
	PT	VE	EP	PH	PMR-15
Reaction	-117.1	-85.7	-113.2	-47.12	-24.18
Carbonization	0.0	0.0	-11.4	-18.8	0.0
Decomposition (Mg(OH)$_2$)	+764.3	+533.4	+561.4	+410.6	+374

Under the same test, pure Mg(OH)$_2$ absorbs about
1147 J/gm during its decomposition reaction.
Therefore, at 66.7% by weight, its absorbs about 763
J/gm. As indicated in Table 8, PT resin optimizes
the heat absorption of Mg(OH)$_2$ during its
decomposition reaction better than all the systems
evaluated.

EXAMPLE 13

Following the procedure described in Example 12,
the effect of filler on thermal decomposition
behavior of the fire retardant system was evaluated.
The resin was a phenolic cyanate and the fillers were
magnesium hydroxide, alumina trihydrate, zinc borate
and basic magnesium. The weight ratio of filler to
resin in the combined system was 2 to 1. The results
are set forth in the following Table 9.

The Effect of Filler on Heat Generation/Absorption
Behaviour

TABLE 9

| Parameter | Part 1: Filler | | | |
	MH[1]	AT[2]	ZB[3]	BMC[4]
1. Water Content (wt%)	31.0	34.5	14	20
2. Decomposition Temperature, C	330	200	300-450	230

| Parameter | Part II: Matrix Filler System | | | |
	MH[1]	AT[2]	ZB[3]	BMC[4]
1. Reaction	-117.1	-120.4	-101.4	-122.0
2. Carbonization	0.0	0.0	0.0	0.0
3. Decomposition $Mg(OH)_2$	+764.3	+708.3	+298.3	+ 600.0

1. "MH" is magnesium hydroxide, $Mg(OH)_2$.
2. "AT" is alumina trihydrate, $Al(OH)_3$.
3. "ZB" is zinc borate, $2ZnO.3B_2O_3.5H_2O$.
4. "BMC" is basic Magnesium Carbonate, $Mg_4(CO_3)_3(OH)_2.4H_2O$.

Example 14

In order to understand the fire resistant behaviour of the system, experiments were performed to determine the change of properties of a fire retardant layer of magnesium hydroxide ($Mg(OH)_2$) and PT resin after carbonization. In these experiments, molded sample were prepared before carbonization using the following procedure:

A small amount (~ 100 gm) of a mixture of PT resin (solids) and $Mg(OH)_2$ (1:2 by weight) was solution (acetone) blended vigorously for 15 minutes using a mechanical stirrer. The mixture was dried in air overnight, and the dried mixture was ground to

powder. The powder was dried further in a vacuum
oven at 30°C for 16 hours at 27" Hg (91.43K pa) to
remove residual solvent. The powder was further

5   reduced with a mortar and pestle and then passed
through a #200 mesh sieves. The powder was placed
into a 3-piece mold with 6 rectangular cavities (1/4"
x 1") (0.635 cm x 2.54 cm) and 6 circular cavities
(3/16" (0.476 cm)). The depth of the cavities was

10 1/16" (0.159 cm). The powder was cured in the mold
at 250°C for 2 hours at 5 tons (4590 kg) pressure.

    The molded samples were carbonized in an oven of
a Thermal Gravimetric Analysis (TGA) equipment under
Argon atmosphere. The materials were first heated

15 from 25°C to 1000°C at a rate of 20 °C/min heating
rate. After the materials were cooled down, the
materials were again heated from 25°C to 1000°C at a
rate of 20°C/min. The carbonized materials were then
evaluated in the following Examples 15 to 20.

20   EXAMPLE 15

    Several experiments were conducted to determine
the effect of the addition of the filler on char
yield of the resin. The resin was a phenolic cyanate

25 (PT), and the filler was magnesium hydroxide
($Mg(OH)_2$). The weight ratio of resin to filler in
the blend was 1 to 2. The char yield was determined
using a DuPont Thermogravimetric Analyzer (TGA). The
sample size ranged from 15 to 25 mg. The scanning

30 rate used was 20°C/min and the sample was heated from
25°C to 1000°C in Argon atmosphere. After the sample
was cooled down to room temperature, the charred
sample was reheated up to 1000°C at the same heating
rate. The result showed only two wt. % loss for the

35 reheated material at 1000°. The result of the char
yield test are set forth in the following Table 10.

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TABLE 10: Char Yield

Char yield (%)

Material	Predicted	Experimental
PT	---------	64.0
$M_g(OH)_2$	69.0	69.0
$PT/M_g(OH)_2$	67.4*	62.0

*$Pc=W_fP_f+WmPm$ (The Rule of Mixture)

EXAMPLE 16

Using the procedure of Example 15, the effect of
the matrix system on char yield was determined. The
filler was magnesium hydroxide ($Mg(OH)_2$ and the
resins was PT, VE, EP, PH and PMR of Examples
1,2,3,4,5 and 6, respectively. The weight ratio of
resin to filler was 1 to 2. The results of the test
are set forth in the following Table 11.

TABLE 11

Char Yield

	Char Yield (%)			
Material--PT	VE	EP	PH	PMR
Value--- 62.0	44.0	47.5	60.0	55.0

EXAMPLE 17

A series of experiments were carried out to
determine the effect of carbonization on the density
of a blend of PT resin and $Mg(OH)_2$ filler where the
weight ratio of resin to filler was 1 to 2. The
density measurement was performed by pycnometry.

Water is used as the testing medium and the
temperature was 23°C. Table 12 summaries the results.

TABLE 12

Density Measurement

	Density(gm/cm^3)	
carbonization:	measured	calculated
(a) Before	1.82	1.93
(b) After	1.62	3.57

*Density(gm/cm^3): M_gO=3.580; $M_g(OH)_2$=2.36; PT
resin=1.05; carbon=3.51

EXAMPLE 18

A series of experiments were carried out to
determine the effect of carbonization on the porsity
of a blend of a phenolic cyanate (PT) resin and
magnesium hydroxide ($Mg(OH)_2$) where the weight ratio
of resin to filler was 1 to 2. The porosity the
sample was determined by X-ray photo spectroscopy
(XPS). The results are summarized in the following
Table 13.

TABLE 13: Porosity

	Porosity(void, %)	
Carbonization	measured	calculated*
	(surface,XPS)	(from density)
(a) Before	6-12	6
(b) After	6-12	54.6

*density(gm/cc): M_gO=3.580; $M_g(OH)_2$=2.36; PT
resin=1.05; carbon=3.51

EXAMPLE 19

A series of experiments were carred out to
determine the effect of carbonization on the

dimension of a blend of a phenolic cyanate resin and
magnesium hydroxide where the weight ratio of resin
to filler was 1 to 2.The results are set forth in the
5 following Table 14.

TABLE 14:   Dimensional Change

<table>
<tr><td rowspan="2">Carbonization</td><td>Thickness (inch (cm))</td></tr>
<tr><td></td></tr>
<tr><td>(a) Before</td><td>0.115 (0.292 cm)</td></tr>
<tr><td>(b) After</td><td>0.104 (0.264 cm)</td></tr>
<tr><td></td><td>Total Change: -9.5%</td></tr>
</table>

EXAMPLE 20

15   A series of experiments were carried out to
determine the effect of carbonization on the thermal
conductivity of a blend of phenolic cyanate (PT) and
magnesium hydroxide, where the weight ratio of resin
to filler was 1 to 2. The thermal conductivity was
20 determined by the differential scaning calorimetry
(DSC) method described in Y.P. Khanna, et al. Polymer
Engineering and Science, Vol 28, No. 16, p 1034,
(1988). The results are summarized in the following
Table 15.

25

TABLE 15 Thermal Conductivity
(method: DSC; unit: W/(MK))

	Temperature Range			
Thermal Conductivity (w/mk) of Filled Resin	50°C	155°C	230°C	330°C
(a)Before Carbonization	1.19	1.10	1.06	0.87
(b)After Carbonization	0.68	0.65	0.50	0.53

The thermal conductivity of pure MgO ranged from
60.0 to 32.0 w/mk at temperatures between 50°C to
35 330°C. The thermal conductivity of the composition
before and after carbonization was considerably lower.

EXAMPLE 21

This example demonstrates the regeneration
capability of the flame retardants at this
invention. The experiment is conducted using thermal
gravimetric analysis (TGA). In this experiment, a
filled phenolic cyanate resin (PT)/Magnesium
Hydroxide (filler to resin weight ratio of 2 to 1)
blend was carbonized as described in Example 11,
converting the $Mg(OH)_2$ into magnesium oxide (MgO) and
water. The carbonized sample was then immersed in
boiling water for 20 hours after which it was
evaluated.

No trace of M_gO was found by x-ray diffraction,
only $Mg(OH)_2$. The regenerated carbonized $PT/M_g(OH)_2$
system shows the same decomposition pattern as the
original $PT/M_g(OH)_2$ system in TGA analysis using the
procedure of Example 12. Flame retardant $PT/Mg(OH)_2$
capacity of the regenerated fire retardant was 97% of
that of the original flame retardant.

WHAT IS CLAIMED IS:

    1. A ballistic resistant article comprising two or
more layers, at least one of said layers being a
fibrous layer comprised of a network of fibers in a
5   matrix, and at least one of said layers being a fire
retardant layer comprising a particulate fire retardant
agent selected from the group consisting of compounds
which exhibit an endothermic effect on exposure to
heat, flame or a combination thereof dispersed in a
10 polymeric layer of one or more thermosetting resins,
one or more thermoplastic resins or a combination
thereof.

    2. A composite as recited in claim 1 wherein the
fibers have a tenacity equal to or greater than about
15 10 g/d, a tensile modulus equal to or greater than
about 160 g/d and an energy-to-break equal to or
greater than about 8 J/g.

    3. A composite as recited in claim 2 wherein said
polymeric matrix has a char yield of at least about 50%
20 by weight of the matrix.

    4. A composite as recited in claim 4 wherein said
aromatic cyanates are selected from the group
consisting of partially cured phenolic cyanate resins
wherein the degree of cure is equal to or less than
25 about 0.50.

    5. A composite as recited in claim 4 said
inorganic compounds are selected from the group
consisting of hydroxides and hydrated compounds.

    6. A composite as recited in claim 5 wherein said
30 fire retardant agent is magnesium hydroxide.

    7. A composite as recited in claim 5 wherein the
particle size of said particulate fire retardant agents
is less than about 1000 microns.

    8. A composite as recited in claim 7 wherein the
35 amount of fire retardant is from about 1% by wgt to
about 99% based on the total weight of the fire
retardant layer.

9. A composite as recited in claim 8 wherein said composite comprises more than one fibrous layer, with adjacent layers aligned at an angle which with respect to the common fiber direction of the parallel fibers

5   contained in said layers dispersed in a polymeric matrix.

10. A composite as recited in claim 9 wherein said angle is from 45° to 90° and said fibers are polyethylene fibers.
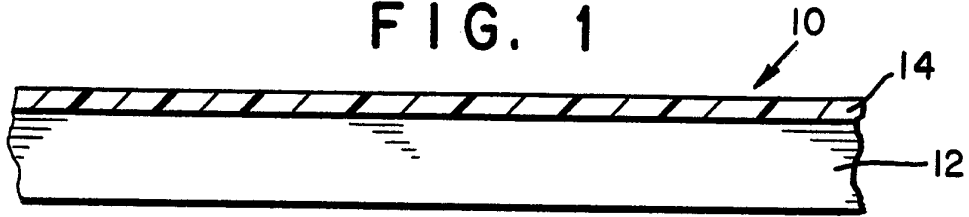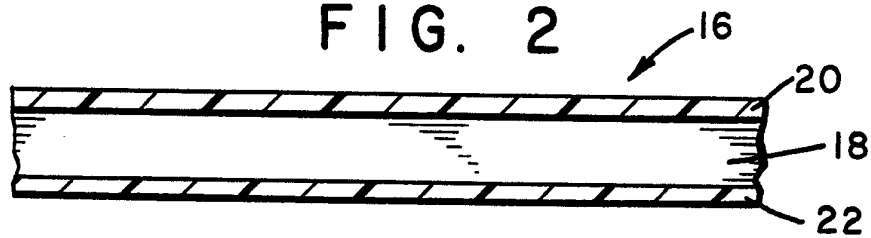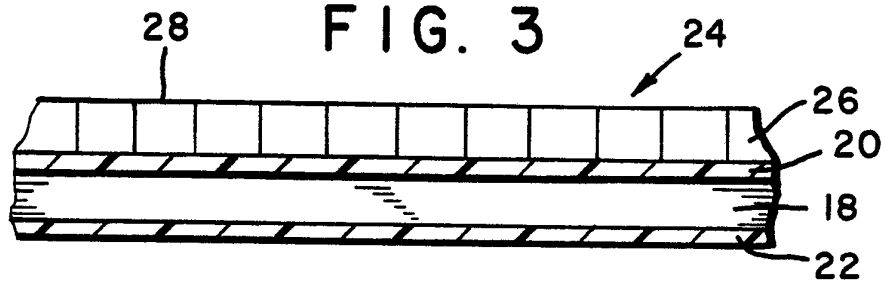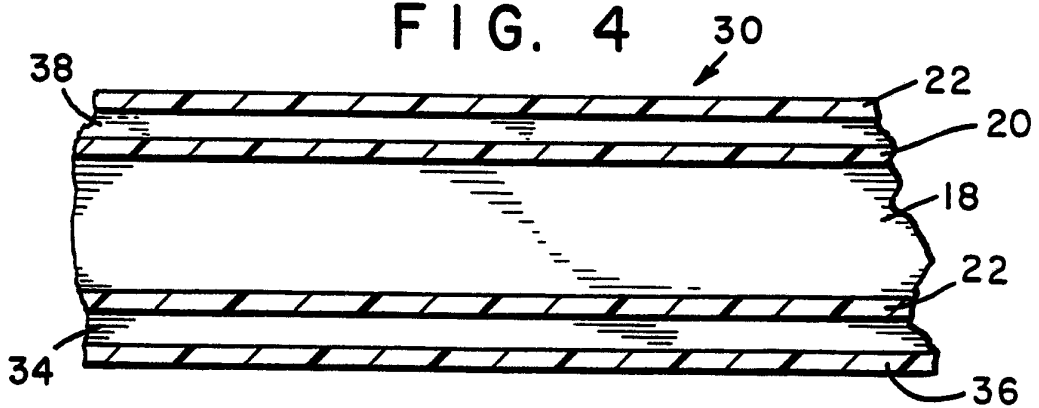
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FIG. 1

FIG. 2

FIG. 3

FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No PCT/US91/09230

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 3

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. CL(5): B32B 5/12 D04H 1/58

US CL : 428/113, 240, 288, 911, 912; 252/602,609

II. FIELDS SEARCHED

Minimum Documentation Searched 4

Classification System	Classification Symbols
U.S.	428/113,240,288,911,912 252/602,609

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 5

III. DOCUMENTS CONSIDERED TO BE RELEVANT 14

Category *	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
A	US,A 4,403,012 Published 06 September 1983	
A	US,A 4,594,290 Published 10 June 1986	
A	US,A 4,748,064 Published 31 May 1988	
X	US,A 4,916,000 Published 10 April 1990, See column 4 lines 37-46, column 5, lines 1-3, column 6, lines 1-6 and Table 2	1-3
X	N. J. Macromol. Sci., issued 1973, Vol. A7(1), R.C. Laible et al, The Application of High-Modulus Fibers to Ballistic Protection, pp. 295-322	1-5 and
Y	US,A 5,006,293 Published 09 April 1991	

* Special categories of cited documents: 15

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

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 2	Date of Mailing of this International Search Report 2
14 May 1992	20 MAY 1992

International Searching Authority 1	Signature of Authorized Officer
ISA/US	Peter A. Nelson

Form PCT/ISA/210 (second sheet) (May 1986)