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(71) Applicant *(for all designated States except US)*: **GREENHILL ANTIBALLISTICS CORPORATION (WY)** [US/US]; 160 East 65th Street, New York, New York 10021 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **GREENHILL, Zachary R.** [US/US]; 160 East 65th Street, New York, New York 10065 (US). **AVNIEL, Yuval C.** [US/US]; 1600 Sherwood Street, Missoula, Montana 59802 (US).

(74) Agents: BOWLEY, Christopher C. et al.; Fish & Richardson P.C., P.O. Box 1022, Minneapolis, Minnesota 55440-1022 (US).

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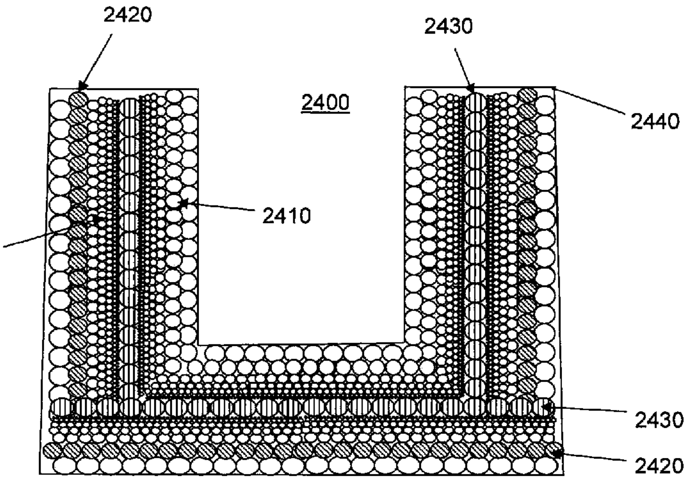

FIG. 24

(57) Abstract: Disclosed herein are engineered composite materials suitable for applications that can benefit from a composite material capable of interacting with or responding to, in a controlled or predetermined manner, changes in its surrounding environment. The composite material is generally comprised of one or more layers whereby each layer is comprised of a plurality of particles having a predetermined median particle size diameter. The predetermined media particle size in each layer, when viewed in cross section, can form a particle size gradient such that the median particle size of each layer sequentially decreases (or increases) across the cross section of the material. Particles can further be core-shell particles releasing their core material upon actuation.

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COMPOSITE MATERIAL

CROSS-REFERENCE TO RELATED APPLICATION(S)

This application claims the benefit of priority under 35 U.S.C. §119(e) from U.S. Provisional Patent Application Serial No. 60/955,335, filed August 10, 2007 and entitled "ENGINEERED COMPOSITE SMART MATERIAL" and from U.S. Provisional Patent Application Serial No. 61/031,913, filed February 27, 2008 and entitled "ENGINEERED COMPOSITE SMART MATERIAL," the contents of which are hereby incorporated by reference in their entirety.

TECHNICAL FIELD

The present invention relates to a composite material and, in particular, to a composite material comprising one or more layers of particles.

BACKGROUND

Material designs for handling the impact of an external stimulus, such as a blast or projectiles, include, for example, woven fabrics, ceramic materials, and composite systems. Kevlar®, Zylon®, Armos®, Spectra® are commercially available fabrics made from high-strength fibers. Another material is ballistic steel, which is comprised of hardened high tensile steel, woven into fiber form. Further, boron carbide can be used as a material, for example, in the production of body armor.

Ceramic materials, in particular ceramic metal composites have found utility in light weight body armor; for examples, the Blast-Tamer wall system from General Plastics Manufacturing Co. (Tacoma, Wash.). The system consists of engineered polyurethane foam panels tied together with adhesive joints and aramid fiber cord, with the space between the panels filled with sand.

SUMMARY

The invention is based in part on the fact that a composite material with a specific gradient layer structure can absorb, distort, and/or redirect a compression wave, such as, e.g., a shock wave accompanying an explosion. In general, composite materials (or composites) are engineered materials made from two or more constituent materials with significantly different physical and/or chemical properties that retain their separate and distinct physical and/or chemical identities within the finished structure.

The invention is further based in part on the fact that a composite material may provide upon activation specific reactions and/or materials to its environment. For example, the composite material and/or at least one of the materials constituting the composite material can be further designed to mitigate and/or remediate primary and/or secondary effects resulting from the compression wave. Thus, some embodiments of the present invention can provide novel composite materials that through intelligent design of the composition of the materials and a structure within the composite material can not only reduce (mitigate and/or remediate) the impact of a shock wave (primary blast effect) with greater efficiency and efficacy but that can also mitigate and/or remediate one or more secondary blast effects. Moreover, the composite material and/or at least one of the materials constituting the composite material can be, for example, further designed to be activated through a chemical signature in its environment or through a physical condition (e.g., of a compression) wave to change a physical and/or chemical property such as color.

The invention is further based in part on the fact that a composite material may use a compression wave to work against itself to mitigate and/or remediate the primary and secondary effects of the compression wave. Similarly, when an incident shock wave is reflected from the composite material, the reflected shock wave can be distorted. When the incident and reflected shock wave form a combined shock wave, primary and secondary effects of the combined shock wave can be mitigated and/or remediated due to the distortion of the reflected shock wave.

In a first aspect of the invention, a multilayer composite material includes a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient.

In another aspect, a multilayer composite material includes a gradient layer structure of a sequence of layers, each of the layers being formed by microscale particles, wherein for the gradient layer structure, a gradient is defined as a change in size of particles populating individual layers.

In another aspect, a multilayer composite system is generally comprised of one or more layers whereby each layer is comprised of a plurality of particles having a predetermined median particle size diameter. The predetermined median particle size in each layer, when viewed in cross section, forms a particle size gradient such that the median particle size of each layer at least sequentially decreases (or increases) across the cross section of the material.

In another aspect, a composite material includes a core-shell particle layer of core-shell particles having a shell surrounding a core material and the shells being in contact with each other (or at least being able to contact each other upon impact of a compression wave) and being configured to release the core material when impacted by a compression wave through momentum transfer from the compression wave onto the shell.

In another aspect, a method includes forming a sequence of particle layers such that a gradient of the particle size over the sequence is defined as a change in size of particles populating individual layers.

In another aspect, a multilayer composite material includes a gradient layer structure that includes a sequence of layers of microscale particles and at least one layer of core-shell particles, wherein the shell of at least one of the core-shell particles is configured to release a core material of the core-shell particle under a threshold physical condition that is controlled by a gradient of the gradient layer structure.

In another aspect, a method includes absorbing energy of a compression wave with a gradient layer structure of microparticles, at least one of which being a core-shell particle, and using the absorbed energy to release a core material from the core-shell particle.

In another aspect, a receptacle includes a transparent gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient.

In another aspect, a liner includes a transparent gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient.

In another aspect, a pipe includes a conductive element, and a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient. The pipe can be used, e.g., for transporting liquids and gases, wherein the gradient layer structure is applied as a cladding, film, or coating, to at least one of the inside surface and outside surface of the piping.

In another aspect, a helmet including a helmet structure, a helmet liner, and/or helmet liner pads includes a gradient layer structure consisting of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, wherein the gradient layer structure is applied to at least one side of the helmet structure, the helmet liner, and/or the helmet liner pads. In addition, or alternatively, the helmet can include a helmet liner which includes the composite material.

In another aspect, a textile includes a cloth, and a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, wherein the gradient layer structure is applied to the cloth.

In another aspect, a transportation device includes a body and a composite material including at least one of a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, and a core-shell particle layer of core-shell particles having a shell surrounding a core material, wherein the gradient layer structure is applied to the body.

In another aspect, a composite material includes at least one of a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, and a core-shell particle layer of core-shell particles having a shell surrounding a core material, wherein the composite material includes a color changing sensor material.

In some implementations of the receptacle, the liner, the pipe, the helmet, the helmet liner, the helmet liner pads, the transportation device, and the textile, the composite material can include, instead of the gradient layer structure or in addition to the gradient layer structure and/or within the gradient layer structure layers of core-shell particles.

Certain implementations may have one or more of the following advantages.

The composite material can be used in various configurations including a coating, e.g., sprayed to an underlying substrate, a film (attachable to surfaces or free standing), a foil, a panel (e.g., molded from the composite material), powder or granular material (e.g., used as a filling material of hollow panels), or any structure made completely or to a large extent from the composite material. Some configurations can include a binding layer on the surface of the composite material. Some configurations can include a binding layer in between layers of the composite material. In addition, or alternatively, an intermediary material can be included within the composite material in between the particles.

In some embodiments, the gradient layer structure can be configured such that a change in particle size between neighboring layers ranges from 5% to 50% of the mean particle size. The particle size of neighboring layers can change by at least 5 %, 10 %, 15 %, 20 %, 25 %, 30%, 35 %, 40 %, 45 %, or 50 %. The particle size of neighboring layers can increase or decrease. For example, the gradient layer structure can include at least a first layer with a first particle size smaller than 1mm and a second layer with second particle size smaller than the first particle size.

In some embodiments, a largest particle layer or a smallest particle layer of the multilayer composite material can be positioned towards an (expected) impact side of the multilayer composite material of a compression wave, thereby providing a decreasing or increasing size of particles in direction of a propagating compression wave.

In some embodiments, a number of contact points per area between particles within neighboring layers can change according to the particle size gradient. The contact points can to some extent be "potential" contact points in a less dense packed layer.

A layer can have any shape and configuration. At least one layer can be a mono-dispersed layer of particles. The thickness of at least one of the layers can be about the mean particle size of that layer. The thickness of at least one of the layers can be larger than the mean particle size of that layer. At least one of the layers can include at least two or more particles in direction of a cross-section of the layer.

In some embodiments, the particles within at least one of the layers can be in contact with each other (or at least being able to contact each other upon impact of a compression wave). In addition, the particles of neighboring layers can be in contact with each other or at least being able to contact each other upon impact of a compression wave.

The particles can be configured for unrestrained movement and therefore interaction upon actuation, e.g., impact of a compression wave. The particles can be loose and unrestrained to allow moving and transferring momentum to neighboring particles.

The particles can include at least one layer of solid particles, hollow particles, core-shell-particles, microspheres, and spherical particles.

The gradient layer structure can include at least one layer with a particle size smaller than 1mm, 0.1 mm, 0.04 mm, 1000 nm, 500 nm, 100 nm, or 10 nm.

The particles can provide essentially elastic interactions between neighboring spheres thereby enabling momentum distribution when transferring momentum from one of the layers to a neighboring layer via the particles. The mass of the particles is configured to allow no delay in reaction to a compression wave.

The gradient layer structure can include at least one layer with a mean deviation below about 1 %, 5 %, or 10 % for a median particle size distribution.

The particles can be dispersed in a resin that allows momentum transfer to neighboring particles.

The gradient layer structure can include an intermediary material, e.g., for binding particles and/or layers together. The intermediary material can fill, for example, at least partially a volume surrounding the particles.

The gradient layer structure can include a pore microstructure, which is at least partially filled with air, gas or an intermediary material. The intermediary material can be a material of the group consisting of ionomers, polymers, polymerizable monomers, resins, and cyclodextrins.

The gradient layer structure can be a first gradient layer structure having a first particle size gradient in a first direction and the composite material further comprises a second gradient layer structure having a second particle size gradient. The first and the second gradient can be directed in the same or in the opposite direction with respect to the layer structure. The composite material can further comprise a third gradient layer structure having a third size gradient in the direction of the first or second gradient structure.

The multilayer composite material can further include a substrate and the gradient layer structure can be applied to the substrate. The substrate can be a housing, e.g., a housing of an electrical device, a helmet, a helmet liner, a helmet liner pad or pads, a waste receptacle, a pad, a frame, a wall, a panel, a waste receptacle liner, a liner, sports equipment such as a racket, a baseball, a golf ball, a thread, textile, cloth, cladding of a pipe, e.g., for a pipeline, and the surfaces of vehicles, vessels and crafts for land, sea, and aviation, etc.

The multilayer composite material can be configured as a self supporting structure. The structure can have the form of a housing, e.g., housing of an electrical device, a waste receptacle, a pad, a frame, a wall, a panel, a waste receptacle liner, a liner, a bag, a foil, sports equipment such as a racket, a base ball, a golf ball, thread, textile, cloth, a helmet, a helmet liner pad or pads, a helmet liner, structural components of vehicles, vessels and crafts for land, sea, and aviation, etc.

The gradient layer structure of the multilayer composite material can be a concentric gradient layer structure around a center particle. The center particle can be a core-shell particle. The center particle can be the inner layer of the concentric layer structure. An outermost layer or an innermost layer of the concentric layer structure can include particles of a largest particles size. Multiple concentric gradient layer structures can be configured as a coating applied to a substrate or as a self supporting article. The concentric gradient layer structure can be attached to and/or applied onto a substrate.

The gradient layer structure of the multilayer composite material can be configured such that a compression wave propagating in the gradient layer structure is distorted. An amplitude of a compression wave propagating in the gradient layer structure can be reduced. The gradient layer structure can be configured such that an impact energy of a compression wave propagating on the gradient layer structure is partially absorbed. The gradient layer structure can be configured such that after reflection of a shock wave a combined shock wave is reduced in destructive power. The gradient layer structure can be configured to mitigate and/or remediate a shock wave. The gradient layer structure can be configured such that when impacted by a shock wave, particles of neighboring layers interact thereby inducing primarily a lateral momentum transfer due to a change in the number in contact points.

The multilayer composite material can further include a core-shell particle layer of core-shell particles having a shell surrounding a core material. Alternatively, or in addition, the gradient layer structure can include such a core-shell particle layer or core-shell particle. The shells can be configured to release core material when impacted by a neighboring particle of the gradient layer structure, e.g., caused by the impact of a compression wave.

At least one particle can contain a polymeric material such as urethanes, vinyls, epoxies, phenolics, styrenes, esters.

At least one particle can contain on or more of ionomers, polymers, polymerizable monomers, resins, and cyclodextrins

At least one particle can contain a fire suppressant of a group consisting of carbonate, bicarbonate or halide salts, telomer based materials that incorporate fluorinated materials, halocarbons, hydrofluorocarbons, hydroxides, hydrates, and polybrominated materials.

At least one particle can contain an agent material for generating a foam, e.g. a polymer foam based on, e.g., urethans, and styrenes.

At least one particle can contain a medical active material such as antibiotics and other medicine for infection, disinfectants, burn relief agents, materials used for medical triage treatment and biological/radioactive mitigating and/or remediative materials.

At least one particle can be a core-shell material and a material of the core, when released, is selected to react with at least one of another core material, a shell material, an intermediary material, and the material of neighboring particles.

Various particles and/or core-shell particles can be configured to provide a staggered chemical reaction, e.g., when impacted be a compression wave.

At least one of the particles includes a radio frequency (RF) shielding material, such as, for example, copper or nickel, cemet, and copper or nickel alloys.

At least one of the core-shell particles can include a shell material containing a polymeric material such as urethanes, vinyls, epoxies, phenolics, styrenes, and esters. The shell material can further include one or more of ionomers, polymers, polymerizable monomers, resins, and cyclodextrins.

At least one of the core-shell particles can include a core material containing a fire suppressant such as carbonate, bicarbonate or halide salts, telomer based materials that incorporate fluorinated materials, halocarbons, hydrofluorocarbons, hydroxides, hydrates, and polybrominated materials.

At least one of the core-shell particles can include a core material containing an agent material such as a polymer foam, urethans and styrenes.

At least one of the core-shell particles can include a core material containing a medical active material such as antibiotics and other medicine for infection, disinfectant, burn relief agents, materials used for medical triage treatment, and biological/radioactive remediative materials.

At least one of the core-shell particles can include a core containing a material, when released, to react with at least one of another core material, a shell material, an intermediary material, and the material of neighboring particles.

At least one of the core-shell particles can include a core containing a material configured, when released, to mitigate and/or remediate a secondary blast effect of an explosion.

A core-shell particle can be a free and unrestricted in its movement.

The shells can be configured to provide the core material at a predefined physical condition. For example, the shell can be configured to rupture at a threshold pressure derived from the pressure accompanying, e.g., shock waves generated by a blast. The shell can be further configured to rupture at a specific pressure caused by the shock wave.

The core-shell particle layer can further include an intermediary material configured to evaporate during impact of the blast wave thereby providing unrestricted movement of the core-shell particles.

A position of a core-shell particle layer in a gradient layer structure can define a minimum strength of an impacting compression wave that is required to initiate the release of the particles.

In a transportation device, the gradient layer structure can be configured as at least one of a coating, a film, and a panel attached, e.g., to an exterior surface. Moreover, the gradient layer structure can be provided within a cavity of a structural component of the transportation device.

The gradient layer structure can be configured to reduce a compression wave to provide a predefined threshold pressure at the core-shell particle layer.

In some embodiments, the composite material is capable of absorbing an impact of a shock wave that, for example, is produced by an explosion or caused during operation of a device. In addition, or alternatively, in some embodiments, the composite material is capable of mitigating and/or remediating one or more secondary blast effects resulting from the explosion.

In some embodiments, the composite material is suitable for use in applications that can benefit from a material capable of interacting with or responding to changes in its surrounding environment. The interaction and/or response can be designed to be performed in a controlled and/or predetermined manner. Exemplary changes in the environment include changes based on variations of mechanical stress (caused by mechanical load, torsional strain, vibrations etc.), pressure, temperature, moisture, pH-value, electric or magnetic fields, and the like.

Examples of applications can include structural materials, ceramics, textiles and antiballistic and anti-shockwave materials. The field of applications can be in civil engineering, aerospace, automotive applications, military, energy and related infrastructure, electronics, sensors and actuators, lubricants, medical applications, and catalysis.

In particular, one can release catalysts upon actuation of the composite material, which can then be used to catalyze materials in various applications. For example, upon impact related fracture of liners or piping or containers, one can design the composite material to release materials that contain spills and clean up via catalysis. Applications include petroleum/oil based piping systems, chemical containers, and refining operations.

Additional applications can include shock wave and/or impact protection of electronic equipment, impact protection in automotive applications and sports equipment, coatings and claddings for buildings or oil pipelines (and the like). Oil pipelines, for example, are confronted with compression waves due to opening and closing of valves. To mitigate and/or remediate, for example, fire or leaking from an intentionally destroyed oil pipeline, the inside surface or the outside surface of the oil pipeline, or both, can further be provided with fire mitigating layers. This can be done alternatively or additionally to compression wave absorbing coating or cladding on the inner or outer surface of the pipeline.

In some embodiments, the composite material is capable of reacting to and/or interacting with one or more stimuli existing in a blast zone environment. For example, in some embodiments the material can absorb at least a portion of an initial blast impact and/or pre-over pressure air wave resulting from an explosion. In addition, or alternatively, the material can be designed to mitigate and/or remediate one or more related blast effects resulting from the blast impact itself. Thus, some embodiments can provide a novel material that through intelligent design of the material systems can not only reduce blast impact with greater efficiency and efficacy but that can also mitigate and/or remediate one or more secondary blast effects.

In some embodiments, the composite material can provide bomb blast mitigation and/or remediation by reducing the reflective value of the bomb blast by absorption of the bomb blast energy. In some embodiments, the primary mitigating and/or remediating process can be by absorption of the bomb blast shock wave. In some embodiments, the mitigating and/or remediating process can be by absorption of the pre-over pressure air wave that precedes the shock wave. Absorption of the shock wave and/or the pre-over pressure wave can occur through one or more mechanisms, including, for example, momentum transfer, destruction of the spatial symmetry of, e.g., the blast wave, plastic deformation, rupture of particles, e.g. filled and unfilled core-shell particles, restitution, and interparticle/interlayer shear.

In some embodiments, the composite material can provides a novel platform from which a wide variety of blast effects can be mitigated and/or remediated. For example, in a core-shell material the absorbed energy can be utilized to rupture, e.g., microcapsules to introduce a series or selection of core materials or material systems into the blast environment and to thus mitigate and/or remediate the blast effects. In some embodiments, the composite material can provide a relatively light weight material that can be applied to pre-existing structures or systems with no deleterious effects on the performance attributes of the pre-exiting structure or system.

In some embodiments, the composite material can offer proactive mitigation by, for example, comprising RF shielding materials that can impede and thereby reduce the possibility of a remote detonation. Furthermore, destructive phenomena can also be addressed through the composite material including remediative solutions to chemical, biological, radioactive, optical, sonic, mechanical failure, and electromagnetic effects.

In some embodiments, textiles, materials of construction, and smart and thin film applications can benefit from the composite material as a multifunctional user defined "smart" material. Exemplary textile applications can include textiles for use in firefighting, law enforcement, military, defense, sports, and fashion. In some embodiments, composite material can be provided in a form such as a cloth or film suitable for forming uniforms, helmets and head gear, or being applied thereto when using them as a substrate that exhibit the beneficial effect of reacting to environmental changes in a predetermined manner. Exemplary uniforms, helmets, and head gear can include those protective uniforms, helmets, and head gear worn by fireman, law enforcement personnel, and military and/or combat personnel.

Examples of composite material applications include further material systems which are designed to utilize latent or introduced energy to perform a multiplicity of internally predictable actions utilizing energy from the system as an energy source for inducing said actions. Applications also exist which utilize the conversion of impact energy (from physical, optical, acoustic, compression etc.) to perform a variety of functions including energy conversion and utilization, actuation of sensors, signals and chemical reactions in a multi-step systems which can, in concert, perform a variety of complex user defined functions.

Some embodiments provide “bomb proof”, impact or smart material applications. Examples of bomb proof applications include receptacles and liners (waste receptacles and bags etc.), construction (buildings and their facades, bridges and their structural members, pipes and pipelines (for fossil fuels, conduits, utilities), automotive (door panels, bumpers, dashboards, windshields and windows, undercarriages and roofs), aerospace (interior/exterior of planes, satellites, helicopters), and high tech (computer/hardware casings, cable protection).

In some embodiments, the composite material can be used in connection with military equipment, structures, vehicles, vessels and crafts for land, sea, and airborne forces to include armored and unarmored vehicles, aircraft, (which includes helicopters and unmanned drones), and nautical vessels such as submarines, ships, boats and the like.

For military and civilian uses, the composite material can be applied as an exterior coating, film, and/or as panel to pre-existing equipment or, alternatively, can be utilized as a composite material for forming structural components of the military vehicle, aircraft, or nautical vessel. Still further, the composite material can also be utilized to provide shielding of electromagnetic radiation (RF etc.) in any of the above-mentioned contemplated applications.

In some embodiments, the color changing sensor material of the composite material can be contained in at least one of the microscale particles, the core-shell particles, an intermediary material, a material of a binding layer, and a material of a binding film of the composite material.

In some embodiments, the color changing sensor material of a composite material can be configured to change color when exposed to at least one of gaseous explosive materials, material components of explosives, materials emitted from an explosive material, vapor of an explosive material, chemical components outgased from an explosive material, and chemical components of an explosive material. The color changing sensor material can be further configured to change color when exposed to vapors signaling the presence of explosive material; either the explosive material itself or a chemical component of a manufactured explosive.

In some embodiments, the color changing sensor material of a composite material can be configured to change color when exposed to a compression wave.

Certain implementations may have one or more of the following advantages. Some implementations can absorb the compression of a bomb blast rather than containing bomb blast within a receptacle. Absorption is more effective as it reduces the destructive power of a bomb rather than contains the destructive power. Some implementations can offer remediation of blast effects. Some implementations can offer a large selection of other functions in situ. Functions can be actuated, for example, in real time by the impinging compression wave. The actuation can be performed at any time. Some implementations can be applied to existing objects and structures without changing initial form or function. Some implementations can be easily augmented to accommodate case specific responses and can be designed to offer user defined properties. Some implementations can be tunable to offer user defined complex and multifunctional performance characteristics. Some implementations can offer a novel material design approach capable of engineering directly into the material a predictable series of responses to an external stimulus, thereby generating a smart material. Some implementations can enable utilizing and combining the properties of individual materials in concert or in series. The details of one or more embodiments of the invention are set forth in the accompanying drawings and the description below. Other features, objects, and advantages will be apparent from the description and drawings, and from the claims.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic cross sectional view of a first composite material with a gradient layer structure having a decreasing particle size in impact direction.

FIG. 2 is a schematic cross sectional view of a second composite material with a gradient layer structure having an increasing particle size in impact direction.

FIG. 3 is a schematic cross sectional view of a third composite material with a plurality of gradient layers structures as shown in FIG. 1.

FIG. 4 is a schematic cross sectional view of a fourth composite material with a plurality of gradient layers structures as shown in FIG. 2.

FIG. 5 is a schematic cross sectional view of a fifth composite material with a plurality of gradient layers structures as shown in FIGS. 1 and 2.

FIG. 6 is a schematic cross sectional view of a sixth composite material with a plurality of concentric particle layers.

FIG. 7 is a schematic illustration of blast environment.

FIG. 8 is a graph of a temporal pressure development in a shock wave.

FIG. 9 is a schematic illustration of a reflection of a shock wave at a seventh composite material.

FIG. 10 is a schematic illustration of momentum transfer in a gradient layer structure.

FIG. 11 is schematic illustration of an exemplary core-shell particle.

FIG. 12 is a schematic cross sectional view of a planar layer structure of mono-dispersed core-shell particles on a substrate.

FIG. 13 is a schematic cross sectional view of a planar gradient layer structure including a core-shell particle layer.

FIG. 14 is a schematic cross sectional view of a concentric gradient layer structure surrounding a core-shell particle.

FIG. 15 is a schematic cross sectional view of a container coated with a composite material as shown in FIG. 1.

FIG. 16 is a schematic cross sectional view of a fiber coated with a composite material as shown in FIG. 1.

FIG. 17 is a schematic cross sectional view of a fiber coated with a composite material as shown in FIG. 12.

FIG. 18 is a perspective view of a pipeline.

FIG. 19 is a perspective view of a hand held device.

FIG. 20 is a schematic illustration of a compression wave deformation in a gradient layer structure.

FIG. 21 is a cross section through a helmet with helmet liner pads, and a helmet liner.

FIG. 22 is a schematic cross sectional view of an exemplary structure of microscale particles for a helmet liner pad.

FIG. 23 is a schematic representation of a transportation device provided at least partly with a composite material.

FIG. 24 is a schematic cross sectional view of an exemplary waste receptacle made from a multilayer composite material.

DETAILED DESCRIPTION

In some aspect, the invention relates to an engineered composite material that is based on several layers of particles with different particle sizes in neighboring layers. Thus, the layers can be arranged to have a (constant or varying) gradient of the particle sizes, e.g., increasing, decreasing, or alternating particle size. Such a gradient layer structure can be capable of absorbing, for example, the energy of an explosion, pressure waves, sound waves, shock waves, and compression waves.

Exemplary gradient layers structures are discussed in connection with FIGS. 1 to 6, 9, 13 to 24. The physical environment generated by a bomb blast is discussed below in connection with FIGS. 7 and 8, and a potential explanation for the effect of the invention is discussed in connection with FIGS. 9 and 10. The presented gradient layer structures provide an increased lateral momentum and energy transfer during propagation of an incident wave. For example, when a gradient layer structure is subjected to the impact of a blast, the shock wave from the blast travels across the gradient layer structure, and it is assumed that the shock wave is increasingly deflected in different directions by the alternating amount of contact points within neighboring layers.

In such gradient layer structures, the particle size can range from about 1 nm to several millimeters, for example, from 150 nm to 1 mm. The material of the particles can comprise, e.g., (porous) silica; aluminum hydroxide; polymeric materials; metal spheres, and ceramics. As shown specifically in FIGS. 3 to 5, a composite material can include several layer structures with identical or reversed direction of the gradient. The layers can be planar or have a specific shape. Moreover, the gradient layer structure can be applied to a substrate having a specific shape, see FIG. 3. Alternatively, the layer structure can be concentric as for example described in connection with FIG. 6.

In some aspects, a composite material includes "filled" particles, for example, core-shell particles such as filled microspheres, see FIG. 11. Depending on the specific application, the shell materials of the core-shell particles can be configured such that given a specific physical pressure, the core material is released. In exemplary embodiments, the composite material can include a mono-layer of core-shell particles or a layer having a thickness of multiple core-shell particles. Exemplary materials for the core can include for fire suppression materials such as potassium bicarbonate, aluminum and/or magnesium hydroxide; for energy absorption porous silica, silica, and/or Perlite; and for RF shielding copper, and/or nickel.

Moreover, in some aspects, the core-shell particle layer can be combined with a gradient layer structure as discussed in connection with FIGS. 13, 14, 17, 22, and 24.

In various applications, the composite materials based on gradient layer structure and/or core-shell particles can be applied to devices such as containers as shown in FIGS. 15 and 24 as examples for waste receptacles. The composite material can further applied to fibers and used in connection with textiles as discussed in connection with FIGS. 16 and 17. Exemplary textile applications can include textiles for use in firefighting, law enforcement, military, defense, sports, and fashion. Such cloth or film can be suitable for forming uniforms, helmets, helmet liners, helmet liner pads etc. that exhibit the beneficial effect of reacting to environmental changes in a predetermined manner. Specific examples can include inner liners for uniforms or jackets that are either attachable or fused into the cloth.

Additional applications, can involve the suppression of compression waves (including shock waves) in pipes. Shock waves are, for example, generated through valve operation in oil pipelines as discussed in connection with FIG. 18. The composite material can further be applied to surfaces that require impact resistance. Examples include housing of hand held devices, helmets, vehicles or components thereof, as discussed in connection with FIGS. 19, 21 to 24. The composite material in those applications can be applied as a coating or provided as a liner. The composite material can further be used in connection with cushions, for example, the helmet pads shown in FIG. 21.

The composite material can be generally comprised of a plurality of adjacent layers whereby each layer is comprised by a plurality of particles having a predetermined median particle size diameter. In gradient layer structures, the predetermined median particle size of each adjacent layer, when viewed in cross section, forms a particle size gradient such that median particle size of each layer sequentially decreases (or increases) across the cross section of the material. The particle size gradient is accompanied by an inverse "gradient" in the amount of contact points per unit of area. For example, a decreasing particle size within the gradient layer structure results in an increase of particle surface contact points per unit of area because more particles interact in each adjacent layer.

The plurality of adjacent layers are configured such that the proximity of the particles within the various layers and the proximity of particles from one adjacent layer to another adjacent layer are sufficiently close to one another to allow a transfer, dissipation, and/or conversion of energy to take place when the gradient layer structure is subjected to the impact energy from, for example, a blast. Specifically, a momentum transfer response only occurs when the particles are touching and compressed. Once the contact between particles is not possible, the particles can become an amalgamation of independent systems which in themselves interact as a multitude of systems.

FIG. 1 shows a schematic cross-sectional view of an exemplary composite material 100. The direction of an impact, e.g., the compression wave of a blast, is indicated through arrow 105 and is directed toward a surface of a composite material 100. The composite material 100 includes a plurality of adjacent layers 110-170. Each of the layers 110-170 of the material includes particles p1-p7 having a predetermined median particle size dp1-dp7, respectively. The relative particle size distribution with respect to the median particle size dp1-dp7 of the particles p1-p7 within any given layer 110-170 is small. For example, the coefficient of variation is below 20%, or below 10%, or even below 5%.

Therefore, each layer of the composite material 100 can be distinguished from the adjacent layer or layers by the difference in particle sizes contained therein. Additionally, within each of the layers 110-170 of FIG. 1, particle surface contact points cp1-cp7 between particles of each of the layers 110-170 are indicated. As can be easily seen, the smaller the particle the more contact points per unit of area.

In FIG. 1, the particle sizes of each adjacent layer form a particle size gradient and satisfy the relationship $dp1 > dp2 > dp3 > dp4 > dp5 > dp6 > dp7$. It should be understood that the specific median particle sizes selected for a given layer of the material are not as critical as long as a desired particle size gradient is provided.

The gradient can be expressed as the change in size of the particle diameters populating individual layers. For example, the particle diameters can shrink (or increase) progressively by a factor spanning the range of 5% and 50%. The shrinking or increasing can be linear or non-linear.

In direction of a decreasing median particle size, the median particle size of the adjacent layers 110-170 can be chosen such that number of particle surface contact points cp1-cp7 per unit area increases at least by one. For example, if one of the layers 110-170 has n particle surface contact points then the neighboring layer having a smaller particles has at least $n+1$ particle surface contact points per unit area. Accordingly, the number of particle surface contact points fulfills the relation: $cp7 > cp6 > cp5 > cp4 > cp3 > cp2 > cp1$.

Microscale particles (e.g. sub-millimeter size particles) can be used to manufacture the composite material and the selection of the size, at least in part, is dependent upon the desired end use application for the composite material. For example, the particle sizes can be less than about 1,000 µm in size, less than about 500 µm, less than about 250 µm, or even less than about 125 µm. Particle size down to the single nanometer scale can be applied.

In case of the composite material 100 of FIG. 1, the particles of layer 110 can have a relative median particle size of about 150 µm, the particles of layer 120 can have a relative median particle size of about 75 µm, the particles of layer 130 can have a relative median particle size of about 40 µm, the particles of layer 140 can have a relative median particle size of about 10 µm, the particles of layer 150 can have a relative median particle size of about 2 µm, the particles of layer 160 can have a relative median particle size value of 0.75 µm and the particles of layer 170 can have a relative median particle size value of 0.15 µm.

The example of FIG. 1 has seven layers. However, it should also be understood that the plurality of layers can comprise less or more layers, for example three or more layers. Examples for the number of layers in a composite material having a gradient in the particle size can include less than seven layers (e.g., two, three, four, five, six), or more layers (e.g. at least ten, twenty, thirty, forty layers). Table 1 shows example layer structures for a gradient of 5 % to a gradient of 50 % starting at a maximum particle size of 40 µm and having up to 40 layers within a gradient layer structure. The indicated median particle sizes decrease layer by layer 5%, 10%, ... 50%. For a gradient of 20%, two layer structures are shown having 20 or 28 layers. Example polymeric particles can include monodisperse polystyrene microspheres and Polybead® Hollow Microspheres. Additional particles and particle materials are discussed below.

Table 1

Gradient	5%	10%	20%	20%	25%	40%	50%
Layer 1	40.00	40.00	40.00	40.00	40.00	40.00	40.00
Layer 2	38.00	36.00	32.00	32.00	30.00	24.00	20.00
Layer 3	36.10	32.40	25.60	25.60	22.50	14.40	10.00
Layer 4	34.30	29.16	20.48	20.48	16.88	8.64	5.00
Layer 5	32.58	26.24	16.38	16.38	12.66	5.18	2.50
Layer 6	30.95	23.62	13.11	13.11	9.49	3.11	1.25
Layer 7	29.40	21.26	10.49	10.49	7.12	1.87	0.63
Layer 8	27.93	19.13	8.39	8.39	5.34	1.12	0.31
Layer 9	26.54	17.22	6.71	6.71	4.00	0.67	0.16
Layer 10	25.21	15.50	5.37	5.37	3.00	0.40	0.08
Layer 11	23.95	13.95	4.29	4.29	2.25	0.24	
Layer 12	22.75	12.55	3.44	3.44	1.69	0.15	
Layer 13	21.61	11.30	2.75	2.75	1.27	0.09	
Layer 14	20.53	10.17	2.20	2.20	0.95		
Layer 15	19.51	9.15	1.76	1.76	0.71		
Layer 16	18.53	8.24	1.41	1.41	0.53		
Layer 17	17.61	7.41	1.13	1.13	0.40		
Layer 18	16.72	6.67	0.90	0.90	0.30		
Layer 19	15.89	6.00	0.72	0.72	0.23		
Layer 20	15.09	5.40	0.58	0.58	0.17		
Layer 21	14.34	4.86	0.46		0.13		
Layer 22	13.62	4.38	0.37		0.10		
Layer 23	12.94	3.94	0.30				
Layer 24	12.29	3.55	0.24				
Layer 25	11.68	3.19	0.19				
Layer 26	11.10	2.87	0.15				
Layer 27	10.54	2.58	0.12				
Layer 28	10.01	2.33	0.10				
Layer 29	9.51	2.09					
Layer 30	9.04	1.88					
Layer 31	8.59	1.70					
Layer 32	8.16	1.53					
Layer 33	7.75	1.37					
Layer 34	7.36	1.24					
Layer 35	6.99	1.11					
Layer 36	6.64	1.00					
Layer 37	6.31	0.90					
Layer 38	6.00	0.81					
Layer 39	5.70	0.73					
Layer 40	5.41	0.66					

In Table 1, a constant gradient of 5 % is given. However, one could alternatively vary the gradient. For example, a gradient layer structure can include the layers 1 to 7 with a gradient of 25 %, followed by layers 35 to 40 with a gradient of 5 %. Additionally, that gradient layer structure can include layers 11 to 28 with a gradient of 25 %

Additionally, a composite material can have a layer structure that includes a series of repeating layer sequences wherein the order of layers within a layer sequence can be inverted and/or the layers of a sequence can be modified.

For example, as shown in FIG.1, any one of the layers 110-170 can include a mono-dispersed layer of particles p1-p7 and thus has a thickness approximately equal to the median particle size diameter of the particles p1-p7 within that layer 110-170. Alternatively, any one or more layers can also be comprised of a plurality of layers of the particles within a given layer. Then, the thickness of a given layer can optionally be greater than the median particle diameter size of the particles within a given layer of the system. Specifically, layers with smaller particles can include, for example, more than one particle, e.g., up to 20 particles.

As further shown in FIG. 1, the energy from a blast impact 105 is directed initially toward the first layer 110 which is comprised of a plurality of particles having the largest median particle sizes. Thus, the energy of the blast impact will then propagate though the material in the direction of largest particle size to smallest particle size, *i.e.*, from layer 110 toward layer 170.

As used herein, the terms "nano" and "nanoscale" particles generally refer to particles having a size on the scale of nanometers, such as, for example, particles having at least one aspect equal to or less than about 100 nm. As used herein, the terms "macro" and "macroscale" particles generally refer to particles larger than nanoscale, preferably particles having at least one aspect greater than about 100 nm, or more preferably particles having at least one aspect greater than about 500 nm. As used herein, the terms "meso" and "mesoscale" particles generally refer to particles having aspects between nanoscale and macroscale systems. As used herein, the terms "micro" and "microscale" particles generally refer to particles from the nanoscale to particles having at least one aspect in the order of thousand micrometers, e.g., in the range of 0.1 nm to 1000 μm.

It should be noted that these sizes and ranges can vary and/or overlap and that therefore the definitions provided herein are intended only to serve as a general guide and not to limit the various embodiments. Nanoscale particles can often exhibit different properties than corresponding macroscale analogs. Mesoscale particles can often exhibit properties that can be attributed to both nano and macro systems.

In some embodiments, the composite material includes macroscale particles, mesoscale particles, and/or nanoscale particles, such that the energy that is dissipated (e.g.

frictional energy) can be increased. In some embodiments, combinations of mesoscale and/or nanoscale particles achieve application specific mechanical properties and the amount of dissipated energy can be increased.

In a composite material, frictional energy dissipation can be increased by populating space devoid of macroscale (large) particles with nanoscale and/or mesoscale (small) particles. The choice of particle size used is a function of a particle size gradient, material composition, and desired properties. The small particles can also be used to adjust the materials mechanical properties (e.g. mechanical strength). In addition, or alternatively, the small particles can introduce further material systems that can be beneficial upon actuation of the system, e.g. by a bomb blast.

It should also be understood that the composite material is not limited only to configurations whereby the layer comprising the largest median particle size forms the surface layer and therefore, receives the initial energy of, e.g., the impact from a blast. For example, as shown in FIG. 2, a composite material 200 can also be formed to comprise the reversed particle size gradient, wherein the first layer to receive the impact energy from the blast is layer 270. According to this embodiment, the energy of the blast impact will propagate though the material along a direction 205 from the smallest particle size to the largest particle size, *i.e.*, from layer 270 toward layer 210. In the gradient layer structure of FIG. 2, the gradient has the opposite direction to the gradient of FIG. 1 and accordingly, the number of contact points decreases for layers being further away from the surface subjected to the impact.

In some embodiments, a plurality of the above described materials can be stacked or arranged sequentially one upon the other. For example, as shown in FIG. 3, a composite material sequence 300 includes a plurality of composite materials 100 (large to small particle size gradient as discussed in connection with FIG. 1) can be stacked or arranged sequentially on top of a substrate 310. Specifically, FIG. 3 shows five composite materials 100. To this end, it should be understood that any desired number of the layer sequence as shown for the composite materials 100 can be stacked or arranged in sequence. Likewise, as shown in FIG. 4, a composite layer sequence 400 includes a plurality of layer sequences as shown for the composite material 200 (small to large particle size gradient as discussed in connection with FIG. 2) can be stacked or arranged sequentially. Once again, it should be understood that any desired number of layer sequences can be stacked or arranged in sequence. A larger number of gradient layer structures and gradient layers can provide self standing structures, while fewer layers or gradient layer structures can provide a flexible composite material that can be applied to structured surfaces.

In some embodiments, and as shown in FIG. 5, a plurality of the composite materials 100 and 200 can be stacked or arranged in an alternating or staggered arrangement to form a composite material 500 so that the interface of two adjacent materials 100 and 200 can comprise either a divergence or a convergence of particle size gradients. Once again, it should be understood that according to this embodiment, any desired number of the composite materials 100 and 200 can again be stacked or arranged in the manner as described.

As illustrated in FIG. 1 to 5, the composite material can be provided as a plurality of substantially parallel or sequential layers which can, for example, be attached, applied or deposited sequentially onto a substrate. However, in some embodiments and as shown in FIG. 6, the plurality of layers can be oriented concentrically, thereby forming a concentrically layered particle 600. The concentrically layered particle 600 includes a central particle 610 that is surrounded by a plurality of concentric layers, only two layers 620 and 630 are shown but many more could be applied. The concentric layers are each comprised of particles of decreasing size as the layers extend farther from the central or core particle 610. As exemplified in FIG. 6, the central particle 610 has a predetermined particle size dp1. First outer concentric layer 620 is comprised of a plurality of particles having a median particle size dp2 that is less than the dp1. The second outer concentric layer 630 is comprised of a plurality of particles having a median particle size dp3 that is less than dp2. Once again, although this embodiment has been exemplified in FIG. 6 as having the central particle 610 surrounded by two concentric particle layers 620 and 630, it should be understood that any number of concentric particle layers can be applied and a central particle is not required and could be replaced by free space or a few contacting inner particles.

It should be appreciated that one advantage of the concentrically layered particles 600 is its potential ease of large scale application. In particular, a plurality of the individual concentrically layered particles 600 can be suspended in a medium and subsequently applied onto a desired substrate. This technique can thus enable the generation of a product with desired energy absorption effect that is based on a single application of concentrically layered particles 600 rather than on a plurality of successive applications of the in order to provide the different layers such as, e.g., the layers 110-170 of composite material 100.

The individual layers which are populated by the different sized particles have a number of distinct attributes. Specifically, the layer thickness can at least for the larger layers be as close as possible to the particle diameter. The reason is that the desired response is a function of the particles interacting. Another way of looking at this parameter is that one wants to maximize the contribution of the particles and minimize the contribution of the other materials.

The particles within the layers must be in a close packed structure, thereby providing the required contact points between the particles or the contacting of particles after being moved only for a short distance (e.g. less then the particle size).

The composite material can be used to mitigate and/or remediate the damage of high intensity compression waves, such as shock waves caused be an explosion. While not wishing to be bound by theory, several mechanisms are presented which are assumed to be responsible for the mitigating features of the composite material.

When an explosive device detonates, it can impact the surrounding environment, in particular the blast zone, through various distinct ways. In particular, as shown in FIG. 7, the explosion of a bomb 10 results in an initial bomb blast with a shock wave 20 of high pressure, i.e., a compression wave, followed by a low pressure zone 30.

The bomb blast can be viewed as a three dimensional wave emanating from the origin of the bomb blast. The leading edge of the blast wave exhibits a nearly discontinuous increase in pressure, density and temperature. The transmission of a bomb blast through a medium is inherently a nonlinear process and can be described by nonlinear equations of motion. Considering an ideal bomb blast produced from a spherical and symmetric source and propagated in a still and homogenous medium, the resulting bomb blast will also be perfectly spherical and therefore the characteristics of the blast wave are functions of a distance R from the center of the source and the time to travel a distance t.

As shown in FIG. 8, the pressure changes across the shock wave 20 and the low pressure zone 30. Prior to the impact of the shock wave 20, at a given point, the pressure is equal to the ambient pressure p_0. At a time t_a that coincides with the arrival of the shock front, the pressure rises discontinuously to a peak pressure of $p_0 + P_s^+$ (over-pressure 800 in the shock wave zone 20). The pressure then decays to ambient pressure in a total time $t_a + T^+$, drops to a reduced pressure $p_0 - P_s^-$ (under-pressure 810 in the low pressure zone 30), and eventually returns to ambient pressure p_0 in a total time $t_a + T^+ + T^-$.

When compression of a medium exceeds the ability of thermal motion to dissipate the energy, the over-pressure 800 occurs. The peak pressure $p_0 + P_s^+$ of the over-pressure 800 can be correlated to the damage produced from the explosion and is considered a primary source of bomb related injuries. Through increasing the over-pressure 800, the reflection of a blast wave from a surface can magnify its destructive power several times. For example, when the shock wave 20 impacts upon a solid surface, it can reflect off the surface and increasing up to nine times in destructive power. Thus, being able to control the reflection of the blast wave based, for example, on coatings of the composite material can allow reducing the destructive power.

The explosion can further result in the formation of a fire ball 40, which trails the blast. Additional secondary blast effects can present distinct threats to life, limb, and property. For example, radioactive materials can cause significant health issues to victims initially impacted by a detonation, along with individuals who later come into contact with blast victims and/or materials exposed to radioactive materials. Chemical agents, such as, for example, nerve, blister, blood, and choking agents, can be released into the environment causing poisoning in people and the environment. Biological materials and/or biological toxins (e.g., Bacillus anthracis), viral agents (e.g., SARS and smallpox), biological toxins (e.g., ricin), or other types of biological materials (e.g., Q fever) can incapacitate, kill, or contaminate the environment.

In the case of electromagnetic weaponry, humans can suffer tissue damage, and electronic systems can suffer irreversible damage. Sonic blasts can rupture living tissue, destroy hydraulic, electronic, and mechanical systems and can propagate large distances from the initial blast source. In addition, other substances can cause a plethora of destructive responses by, for example, malicious intent or natural tendency. Although not shown, another blast effect is caused by accelerating particulate material and shrapnel that can also result from the force of the blast.

As described below in connection with, for example, FIGS. 11-24, an embodiment of a composite material can be configured to mitigate and/or remediate one or several of those secondary blast effects. The composite material can be active independently or in combination with a gradient layer structure.

While not wishing to be bound by theory, several mechanisms are explained in connection with FIGS. 9 and 10. As illustrated in FIG. 9, the mechanisms are considered to contribute to the reduction of the destructive power of a shock wave 910 when reflected from a composite material 900 with a gradient layer structure. Exemplary mechanisms include energy absorption, wave dispersion, and braking of the wave symmetry.

In FIG. 9, a reflected shock wave 920 is illustrated to have a reduce amplitude corresponding to an energy absorption mechanism during reflection. The energy absorption can be based on internal friction (due to shear forces between the layers), inelastic interaction between particles, and/or the breaking of particles or particle shells.

In addition, the reflected shock wave 920 can be stretched in time (as shown), e.g., dispersed due to a modified momentum transfer mechanism based on the gradient structure as discussed in connection with FIG. 10. The propagation of the shock wave in the direction of arrow 1005 through a gradient layer structure 1000 depends specially and temporally on the momentum transfer between the particles of the various layers of the gradient layer structure 1000. As indicated in FIG. 10 through double arrows 1020, momentum can be transferred between particles of the same layer. A momentum transfer between particles of neighboring layers is in general not parallel to the propagation direction of the shock wave through the composite material. Arrows 1030 indicate the momentum transfer direction between particles of neighboring layers, which is given through the contact points of those particles. Thus, the momentum associated with the impacting shock wave can be redirected and then partially absorbed within the layers. Based on the large number of contact points and momentum transfer events, the increased particle numbers in the layers with the smaller particles are assumed to contribute significantly to the reduction in energy.

Moreover, as explained in connection with FIG. 20 the symmetry of a wave front 2000 of, e.g., a shock wave can be distorted during propagation within a gradient layer structure 2005 along a direction 2010 of propagation. FIG. 20 shows a sequence of schematic illustrations of the wave front 2000 at four positions within the gradient layer structure 2005. Four schematic drawings 2006, 2007, 2008, and 2009 of the gradient layer structure 2005 illustrate additionally the location of four increasingly distorted wave fronts 2001, 2002, 2003, and 2004. Layers with black spheres correspond to the position of the wave front within the gradient layer structure 2005.

As shown in FIG. 20, the incident wave front 2000 is assumed to be essentially a planar wave that is well defined and has a large amplitude (shock wave). In FIG. 20, the magnitude of the amplitude is illustrated by the thickness of the lines representing the wave front.

Within the gradient layer structure 2005, the wave front of the compression wave becomes distorted. Specifically, when interacting with particles of various sizes of the various layers of the gradient layer structure 2005, and, in particular, when advancing from one layer to another, the planar form of the wave front is distorted.

For example, and while not wishing to be bound by theory, at some locations in the plane of the wave front, the shock wave propagates slower than at others. For a first layer

2011 of the gradient layer structure 2005, the upper and lower parts of the wave front 2001 are delayed. Thus, in the first layer 2011, the spatial extent of the compression wave in the direction 2010 of propagation increases to a spreading A.

When the wave front reaches a second layer 2012, a third layer 2013, and a forth layer 2014, the wave front is spread accordingly over larger and larger spatial extents B, C, and D. As the distorting affect of the gradient layer structure extends over the complete wave front, the shape of the wave front is distorted at all spatial positions within the "surface" of the wave front, which is illustrated by the large positional fluctuation in the direction of propagation of the wave front at the forth layer 2014.

At the same time, the amplitude of the compression wave is reduced during propagation of the wave front from layer to layer indicated through thinner lines for the wave fronts at subsequent layers. Thus, the form of a compression wave can be perturbed and stretched. Disruption of the wave form can further assist in diminishing the destructive potential of a reflected wave. For example, it causes destructive interference of a reflected and not-reflected part of the shock wave, thereby reducing, for example, the combined danger of bomb blasts close to reflecting surfaces.

As explained in connection with FIGS. 7 and 8, a shock wave resulting from an explosive blast can take the form of a sharp change in gas properties on the order of a few mean free paths, for example micrometer scale changes in thickness at atmospheric conditions. While not wishing to be bound by theory, the percentage of energy lost or dispersed as a wave travels across a composite medium based on loose particles is not as dependent on the size and velocities of the particles. The mechanisms can be a function of the number of particles across the gradient and the amount by which the particles average size successively decreases across the gradient. Thus, the normalized kinetic energy of a wave can be assumed to decay with the number of particles present in the composite material. Factors intrinsic to a compression wave that can influence the propagation characteristics of a wave impacting a composite material can include further, for example, energy flux, intensity, and pressure associated with the compression.

The reduction in energy of a compression wave can vary for any particular embodiment of a composite material. In particular, the reduction in energy, in accordance with the various embodiments, can be a function of one or more of the proposed contributing mechanisms. The level of energy reduction within a composite material can be analyzed by determining the contributions from, e.g., the energy dissipated by molecular friction in view of the potential, kinetic and surface energies within the system, by rupture of the particles, and redirection of the momentum thereby reducing. While not wishing to be bound by theory, the level of energy reduction resulting from the at least partial destruction of the spatial symmetry can be, for example, a function of the number of layers of graded particles, the differences in median particle sizes and masses, and other particulars of the wave form itself.

An energy balance analysis as a function of particle to particle interaction can be calculated by determining: the geometry of each particle, Poisson's ratio, Young's modulus and inter granular surface contact area. For two perfectly spherical particles having radii R_1 and R_2, and shared contact surface C_{12}, the energy between the two spheres can be expressed as a function of contact area:

$$Energy_{c_{12}} = \frac{8}{15}\left(\left(\frac{1-\sigma_1^2}{E_1}\right)+\left(\frac{1-\sigma_2^2}{E_2}\right)\right)^{-1}\sqrt{\frac{R_1R_2}{R_1+R_2}} * C_{12}^{5/2}$$

wherein σ is Poisson's ratio, E is the Young's modulus, and subscripts 1 and 2 refer to the individual grains. Poisson's ratio, as used herein, is defined as the ratio of the relative strain normal to the applied load (transverse strain) divided by the relative strain in the direction of the applied load (axial strain). Young's modulus, as used herein, is defined as a measure of the stiffness of a material, and is also known as the modulus of elasticity, elastic modulus or tensile modulus.

Thus, a reduction in energy can be related to real time effects, such as, for example, a reduction in shock wave amplitude, shock wave over pressure, area of fragmentation, area of blast damage, the relative destructive power of the shock wave, and changes in the mechanical energy generated by the blast. In various embodiments, order of magnitude reductions in each component can be expected.

In other words, when subjected to the impact of a blast, the impact energy from the blast travels across the gradient and is increasingly deflected in different directions by the interaction with the increasing number of contact points. This multidirectional deflection results in a net reduction of energy as the directional components increasingly cancel due to opposing directional components. The deflection due to a size gradient in the average particle sizes of a layer can also cause breakdown in the translational symmetry of the impact wave, further resulting in a reduction of energy.

As exemplified schematically in FIG. 10, as the impact energy comes in contact with ever decreasing particle sizes the impact is differentiated into an ever increasing amount of separate energies each with a distinct vector quantity, characterized by its magnitude and direction. As the direction of the impact energy travels across the gradient it is then deflected in different directions. The deflection results in a net reduction of energy as the directional components increasingly cancel due to opposing directional components.

Further, the impact energy could also dissipate through inter-granular friction, re-orientation of momentum transfer and the resulting shear forces within the composite material as the compression wave traverses the composite material causing re-orientation of the particles.

In addition, a blast wave is also disrupted as a result of a breakdown of translational symmetry, a reduction in the blast wave energy due to increasing attenuation, or a combination thereof.

While not wishing to be bound by theory, in one embodiment a compression wave traveling across a composite material can be squeezed due to the reduction in grain size across the gradient of a material, resulting in at least the partial destruction of the spatial symmetry of the wave. This can also be expressed as a breakdown of translational symmetry, wherein a solitary wave loses its reflection symmetry and is diminished and/or destroyed. In one specific embodiment, such a breakdown in translational symmetry results in a significant reduction in energy.

In another specific embodiment, such a breakdown in translational symmetry results in a destruction of a wave. In another embodiment, the translational symmetry relates to the momentum conservation law, as described by Noether's theorem. As momentum must be conserved, the speed of the smaller particles will increase, and thereby disrupt the wave form, thereby reduce the increase of the destructive power of the wave e.g. upon reflection.

As the leading edge of an impact wave advances on progressively smaller particles having less mass, the smaller particles can, in various embodiments, move at a faster rate than the larger particles, resulting in a change in the propagation of the wave. Such a change can be, for example, in the form of a non-linear increase in wavelength (stretching) of the wave, a non-linear change in the wave amplitude, and/or a change in the waveform itself. As the waveform changes, the wave can, in various embodiments, experience a decrease in kinetic energy and an increase in frequency. The increase in wave form frequency, in turn increases the attenuation of the particles experiencing the waveform. The maximum attenuation achievable for a particular system can depend on, for example, the radii and number of individual grains in the system. Thus, through the selection of materials, it can be possible to create a specific level or system of attenuations for a wave.

Changes, such as increases, in the attenuation of a wave can assist in the dissipation of a wave's energy. For example, the frictional dissipation of energy for larger, e.g. macroscale particles can be on approximately the same scale as collision energy dissipation. For mesoscale and nanoscale particles, the frictional dissipation can be greater than the collision energy dissipation.

In various embodiments, composite materials can provide engineered material systems, enabling the utilization of elastoplastic and finite plastic deformation regimes, while providing control over reflection of the stress wave propagation to effectively dissipate shock wave progressions.

The effect of a composite material can also be viewed based on the propagation of the shock wave. Waves are transmitted through gases, plasma, and liquids as longitudinal waves, also called compression waves. Through solids, however, waves can be transmitted as both longitudinal and transverse waves. Longitudinal waves are waves of alternating pressure deviations from the equilibrium pressure, causing local regions of compression and rarefaction, while transverse waves in solids, are waves of alternating shear stress. Shear stress is one way in which our invention reduces the energy of the wave.

Matter in the medium experiencing the wave is periodically displaced by the compression wave. The energy carried by the wave can convert back and forth between the potential energy of the extra compression (in case of longitudinal waves) or lateral displacement strain (in case of transverse waves) of the matter and the kinetic energy of the oscillations of the medium.

In regards to kinetic energy, a propagating wave moves the molecules in the medium which is carrying it, i.e. compression and rarefaction as the wave travels through the medium. In order for the compressions and rarefactions to occur, the molecules must move closer together (compression) and further apart (rarefaction). Movement implies velocity, so there must be a velocity component which is associated with the displacement component of the wave. The resulting velocity is a function of the materials (packing structure, density, stiffness, mass, inertia). Pressure is a scalar quantity and has no direction; pressure relates to a point and not to a particular direction. Velocity on the other hand is a vector and must have direction; things move from one position to another. It is the velocity component which gives a wave its direction. The composite material changes and/or splits the velocity vector as a function of particles impinging upon one another, thereby reducing the energy in the system.

The velocity and pressure components of a wave are related to each other in terms of the density and springiness of the medium experiencing the wave. A propagating medium which has a low density and weak spring would have a higher amplitude in its velocity component for a given pressure amplitude compared with a medium which is denser and has stronger springs.

Mechanical waves originate in the forced motion of a portion of a deformable medium. Mechanical waves are characterized by the transport of energy through motions of particles about an equilibrium position. In case of the composite material, particles of a first layer subject to an incoming compression wave are accelerated by the change in pressure and pushed in the direction of the second layer. As one layer of the composite material after the other is affected, the wave progresses through the medium. In this process the resistance offered to deformation by the consistency of the composite material, as well as the resistance to motion offered by inertia, must be overcome. As the disturbance propagates through the composite material, it carries along amounts of energy in the forms of kinetic and potential energies. The transmission of energy is affected because motion is passed on from one particle to the next and not by any sustained bulk motion of the entire medium.

Deformability and inertia are essential properties of a medium for the transmission of mechanical wave. If a medium were not deformable, any part of the medium would immediately experience a disturbance in the form of an inertial force, or acceleration, upon application of a localized excitation.

When the grain diameters progressively shrink in radius by some factor, the spatial symmetry of the solitary wave is destroyed. The leading edge of the wave is assumed to travel progressively faster whereas the trailing part of the wave is assumed to travel progressively slower. This is due to the lighter mass of the smaller particles moving faster than their larger neighbors. Thus, it is assumed that progressively less energy is carried by the leading edge.

Thus, the resulting lag and/or compression of a shock wave 20 traveling through a composite material can be used to muffle the shock wave 20 within the composite material and, when used with, e.g., elastic materials, can provide a mechanical and/or electrical/magnetic advantage.

The induced change in the wave form can be utilized to provide a smart material that, for example, allows utilizing a specific change in the wave form to actuate mechanical sensors or actuators incorporated into the material or those incorporated into or on the substrate upon which the invention is coated. As an example, the shock wave can be used to provide an electrical stimulus to piezoelectric materials, which in turn can actuate a variety of electrical systems.

Returning to the structural features of the composite material, it should be appreciated that the plurality of particles can provide a level of porosity within the composite material that depends on the particle size. Thus, the composite material can includes voids or spaces where particle contact points do not exist. The porosity can be a continuous pore microstructure within a given layer of particles or even throughout the entire composite material itself. Alternatively, the resulting pore microstructure can also be discontinuous with respect to a given layer of particles and even discontinuous throughout the entire material itself.

The level of porosity (continuous, discontinuous, or a combination thereof) can affect material properties. When producing a composite system layer by layer, one can provide a layer specific porosity. In addition, the size of the pores differs in individual layers along the particle size gradient. The varying densities within the composite material can further perturb a compression wave (amplitude, frequency, spatial form).

In some embodiments, no binding layer or intermediary material between the particles is required to hold the composite material together. In some embodiments, nanoscale and mesoscale particles but also some macroscale particles can provide surface interaction that does not require a glue-like binding material and nevertheless provides the particle sufficient mobility for momentum transfer.

For example, in some embodiments, functionalized polymer based microparticles of alternating layers can provide carboxylic acid and amine groups on their surface. The coupling between the acid and base functionalities can be used to bind the layers.

In addition or alternatively, based on an adjusted pH value during manufacture of the composite material, one can use electrostatic interactions to bind the layers of microparticles.

In some embodiments, some of the microparticles can carry their own binder. For example, microparticles of one of the layers, can be functionalized with a hydrophobic coating, which is configured to hold the microparticles to a hydrophobic (polymer) surface. Thus, such a layer can build up an attractive force to a neighoring layer of polymeric microparticles. Thus, alternating layers within the gradient layer structure can be coated and non-coated to form the composite material.

In some embodiments, charged particles can be based on an ionomer (charged polymer) as a binder. If microparticles are positively charged using a functionalized coating, a layer of microparticles can be followed by a layer of ionomer microparticles that binds the next layer.

The above implementations to hold particles together can be applied to the complete composite material or only to layers of smaller (nanoscale and/or mesoscale) particles. The implementations can be applied between layers of microparticles as well as within one layer between particles. Within a composite material, the implementations can be used together if feasable or vary within the composite material.

In some applications, one will need to complement the composite material with an intermediary material, which can be within the composite material, and/or with a binding layer (a top layer or a layer between layers), such that at least some of the microparticles (e.g., the larger microparticles of the layer structure) or all microparticles are held together.

For example, a polymer filling, e.g. polymerizable monomers, a resin filling and/or cyclodextrin filling can be used as a intermediary material. The cyclodextrin can act in a similar manner as the above discussed ionomer. The cyclodextrin does not need to fill the pore microstructure completely and uses electrostatics to bind microparticles.

In some embodiments, a resin can fill the pore microstructure and add to some extent or even increase the thickness of a layer. Between layers, one can also add a polymer film that can be made as thin as several nanometers thereby adding slightly thickness to the layer structure. Intermediary materials can be used to fill the accessible volume. For example, the porosity of the composite material 900 in FIG. 9 can at least be partially filled with an intermediary material 950. In general, the intermediary material can span a portion of at least one particle layer, span an entire particle layer, or can even span the entire composite material. The intermediary material can provide some kind of support for the particles without essentially affecting the mobility of the particles and the involved momentum transfer between particles.

The selection of an intermediary material can depend, at least in part, upon the particular desired effect and the particular end use application for the composite material. For example, one can introduce oil into the porosity of the composite material using capillary effect. Intermediary materials can, for example, be utilized to alter the energy absorption characteristics of the composite material. For instance, the intermediary material can be used to augment the compression behavior of the material.

Alternatively, or in addition, a fire retardant can be incorporated into the system as an intermediary material. Moreover, examples for an intermediary material can include materials that when combined via pressure and temperature, interact with the surrounding material to change the characteristics of the resulting material to produce foam, aerogel, solgel etc.

Furthermore, the intermediary material can change the density of a given layer to further disrupt the wave form of the compression wave. The intermediary material 950 can further change the stiffness of the composite material 900, thereby allowing the composite material to be free standing, for example. The intermediary material can further be used to impart cosmetic or aromatic value to the composite material.

In any of the composite materials illustrated in the drawings, intermediary material can in principle be used or it can be applied either in whole or in part throughout the structure.

In addition to the energy absorption properties provided by the gradient layer structure, the composite material can include core-shell particles 1100 as shown in FIG. 11. The core-shell material 1100 includes a core-material 1110 within a shell 1120. Examples for a core-shell particle 1100 include filled microspheres (or spheres) and other encapsulating particles that encapsulate one or more core material 1110. In some core-shell particles the core is hollow. The thickness of the shell 1120 can be, for example, between 30 % and 1 % of the diameter of the core-shell particle 1100. The core material can fill the encapsulated material completely or partly. Further, combinations of materials can be encapsulated. The score-shell particle can be a microscale particle. In some embodiments using a large amount of a specific core-materiel, the core-shell particles can have a diameter of several millimeters.

The shell material of the shell 1120 can be pliable such that the shell 1120 can deform, e.g., upon impact of a compression wave of a bomb blast. The shell material of the shell 1120 can in addition or alternatively be pliable such that the shell 1120 can deform when subjected to, for example, over pressure.

The core-shell particles (as well as the particles in general) can be spherically or asymmetrically shaped. The shell 1120 can be a continuous wall surrounding the core or can be designed to have droplets of the core material embedded through the microcapsule.

Upon impact of a compression wave, the particle shells 1120 within an impacted layer can deform such that a portion of the energy associated with compression wave is therefore absorbed by the core-shell particle. As the shell 1120 deforms, it can also apply pressure to particles adjacent to it, thus transferring a portion of the impact energy to the energy required for subsequent deformation and angular pressure on neighboring particles.

Moreover, to provide specific features in a, pre-blast environment, for example, the core material can be configured to have various features. For example, it may operate as RF shielding to impede remote detonation of bombs.

Additionally, or alternatively, the core material 1110 can, for example, include an agent material (e.g., a secondary blast agent), the presence of which can be utilized to interact with secondary blast effects in a post blast environment in a predetermined manner. For example, in one embodiment, the core-shell particles 1100 can encapsulate one or more agent materials capable of mitigating and/or remediating secondary blast effects, such as flash, fire, chemical agent release, biological agent release, radiation release, and shock wave caused damages. To that end, agent materials can include without limitation, fire retardants, flash suppressants, medicinal treatments, and the like.

The core-shell particle 1100 can also encapsulate one or more agent materials that when combined through actuation or actuation and rupture, can interact with each other or with the blast environment to produce a desired effect. For example, in one embodiment it is contemplated that separate agent materials can be encapsulated such that when combined through rupture of several core-shell particles 1100 the materials react to generate fast setting structural foam. Such foam can, for example, assist in mitigating and/or remediating oil loss from ruptured pipelines as explained in connection with FIG. 18 below.

In use, the shell 1120 of the core-shell particle 1100 can deform under the impact pressure from a shock wave to a deformation where shell rupture occurs, thus releasing the core material 1110 as an agent material, e.g., a secondary blast agent, which is thereby directly released into the blast zone. The released agent materials can then directly interact with the environment to mitigate and/or remediate, e.g., one or more secondary blast effects.

Moreover, it is contemplated that by exposing an agent material to a combination of relatively large pressure and heat changes, the released agent material can, for example, be consumed in or can otherwise participate in a reaction that produces further reaction products that can also be beneficial to remediation and/or mitigation of blast effects.

As shown in FIG. 12, core-shell particles can form a composite material 1200 that can be applied as a coating or as a film to a substrate 1210. The composite material 1200 includes three mono-dispersed layers of core-shell particles 1220, 1230, and 1240. The core material of the layers 1220 and 1240 is indicated to be the same (vertical hatching) and to be different from the center layer 1230 (diagonal hatching). Under certain conditions, e.g., under high pressure caused by an explosion, the shells of the core-shell particles rupture and release the core material. The core material can provide mitigation for itself and/or in combination and/or after reaction with each other. The functionality of the composite material 1200 can thereby be adapted to the specific application.

Thus, as shells rupture in successive layers, agent materials contained in different core-shell particles can be sequentially introduced into the blast zone allowing more complex systems to be introduced and allowing sequential reactions to occur in a predefined manner. This staggering of additional agent materials (secondary agent materials, tertiary agent materials, quaternary agent materials, etc.) in a pre-designed manner can further allow sequential reactions whose sum reaction is greater than their individual contributions.

The composite material 1300 of FIG. 13 includes a single mono-dispersed core-shell particle layer 1310, a gradient layer structure 1320, and a substrate 1330.

The gradient layer structure 1320 includes a mono-dispersed layer 1340 made of core-shell particles. Thus, the advantages of the gradient layer structure can be combined with the advantages of the core-shell particles. This allows further adapting threshold conditions within the gradient layer structure for the release of the core-material.

Similarly, core-shell particles can be included in concentric gradient layer structures. In Fig. 14, a composite material 1400 includes as a center particle a core-shell particle 1410. A layer 1420 having a thickness of multiple particle diameters is formed around the core-shell particle 1410. Then, three concentric layers 1430, 1440, 1450 consisting of mono-dispersed particles of increasing size are applied. An intermediary material 1460 provides structural cohesion of the particles.

Based on the above described composite materials, exemplary applications are described in connection with FIGS. 15-19, and 21-24.

FIGS. 15 and 24 illustrate the application of the composite material in the context of waste receptacles. In FIG 15, the composite material is attached to a support structure of a container 1500, forming for example, the structural basis for a waste receptacle. The inner surface of the container 1500 is coated with a gradient layer structure 1510. The gradient layer structure is representative for various configurations of the composite material, specifically, combinations of gradient layer structures and core-shell particle layers as discussed within this application, for example, in connection with FIGS. 3-6, 9, 11-14, 22, and 24. Thus, any explosion initiated within the container 1500 and generating a shock wave is reduced in its destructive power because the shock wave looses intensity when traveling through the gradient layer structure and when reflecting from the coated walls of the container 1500. Additionally or alternatively, the outer surface of the container can be coated with a gradient layer structure.

Moreover, instead of being applied as a coating, the composite material can be attached as a film or panel. In some configurations, the support structure can be only a frame and the composite material forms, for example, transparent walls to that frame.

Alternatively, or in addition, the waste receptacle itself may consist entirely of the gradient layer structure as will be discussed below in connection with FIG. 24.

Moreover, the composite material can be transparent, opaque, or non-transparent and it can be manufactured, for example, as a film or as a bag, e.g., a waste receptacle liner. Moreover, it can be made as individual bags or in rolls, which separate at serrations. The film can be applied onto a substrate of any shape. The composite material can mitigate and/or remediate by absorption and dissipation in a predetermined manner, for example, effects of a bomb blast, which originates on either side of the composite material. In addition, the composite material can use the shock wave to mitigate and/or remediate the bomb blast by rupturing and/or vaporizing core-shell materials, such as microcapsules, which populate the gradient layers as one of the gradient layers or as a layer attached to the gradient layer structure. The core-shell materiel can be hollow or filled with material (core-material), concentric and/or non-concentric as discussed within this application.

Materials suitable as core material for core-shell particles of a core-shell particle layer, e.g., next to a gradient layer structure 1510 or forming a layer within the gradient layer structure 1510, include flame retardants and suppressants, foam-generating materials and dispersants, materials which suppress and/or deform acoustic waves, materials which suppress smoke and dust, for example. The core material can further contain materials associated with medical treatment, for, for example, burns, infection, inflammation, pain, antibiotics, and materials used for triage medical treatment, materials which impede RF transmission, and/or electrical impulses, in order to reduce the risk to first responders from secondary devices placed and planned to be activated by remote signal, and material which impede the dispersal of biological and radioactive agents.

The composite material can further contain a sensor material that changes color when activated by a specific chemical signature of matter in its environment, e.g., carried by solid particles, gases, and/or liquids. The sensor material can be contained in the particles of the composite material, e.g., in filled or hollow microspheres and/or core-shell particles of the gradient layer structure 1510 and/or a core-shell particle layer (e.g., core-shell particle layer 2220 in FIG. 22). The sensor material can additionally, or alternatively be contained in a film or coating material, e.g., forming an outside surface of the composite material. Moreover, in addition, or alternatively, the sensor material can be contained in a binding layer (e.g., binding layer 2440 in FIG. 24) and/or in an intermediary material of the composite material (e.g., intermediary material 950 of in FIG. 9).

For example, explosives that release a (gaseous) material with a specific chemical signature can yield a concentration above a predetermined concentration in, e.g., a closed or partly closed waste receptacle. Then, the sensor material acts as a (chemically triggered) sensor and identifies the presence of the explosive in the waste receptacle by changing its color. The composite material with the sensor material can be part of a waste receptacle or of a waste receptacle liner or any structure subject to be used for hiding an explosive.

Example sensor materials for detecting explosives such as C-3, SemtexH, and TNT include a mixture comprised of zinc, glacial acetic acid and the NitriVer 3 Reagent supplied, e.g., by the Hach Co. (Cat # 1407899). These materials can be combined in solution with water and can then be applied as a sensing film that is dried onto the gradient layer structure, onto the core-shell particle layer, and/or in between particle layers. In addition, or alternatively, these materials can be presented separately as, e.g., microscale particles (such as nanoscale particles) or coatings on microscale particles (such as nanoscale particles) in the gradient layers. Example particles that can be coated include, for example, zinc particles and polymer particles with acid groups. Moreover, the materials can be provided as a shell material of a core-shell particle. The reaction and detecting of, for example, TNT or RDX can be performed as described in The reaction and detecting of, for example, TNT or RDX as described above can be adapted from the method as described in EPA METHOD 8510 "COLORIMETRIC SCREENING PROCEDURE FOR RDX AND HMX IN SOIL" Revision 0,, U.S. Environmental Protection Agency, February 2007 (http://www.epa.gov/SW-846/pdfs/8510.pdf), the contents of which are hereby incorporated by reference in their entirety.

The inner layers of the composite material 1510 provide gradient layer structures with particles in size and sequence such that a distortion of the compression wave is achieved. Moreover, the reflected wave can be distorted and/or diminished such that, for example, the primary and secondary effects of the combined compression wave (based on the reflected wave and the initial compression wave of the bomb blast) are at least to some degree mitigated and/or remediated.

An inner layer of the composite material, with which a person usually cannot get in contact, can also include particles (microparticles, core-shell particles etc.) that contain a rodenticide for, e.g., rat control. In case of a bomb blast, the rodenticide vaporizes and/or incinerates and would not harm the environment. The layers, which contain the rodenticide, can be changed by generation of manufacture to account for the evolution of immunities in the area's rodent population.

As noted above, the composite material 1500 and the composite material 2400 can alternatively, or in combination, also be implemented in a liner that is used with a waste receptacle or used as a separate bag for waste material.

When, for example, a bomb detonates within the container (waste receptacle), by the use of a timing device, (because RF shielding makes detonation by a radio signal sent to a cell phone or other radio receiver at the bomb ineffective), layers of the composite material closest to the detonation absorb the blast energy and cause rupture of the core shell particles within the composite material, which release their contents. As the shock wave moves through the composite material, to the inner layer particles, deformation of the shock wave increases.

Further, as the shock wave propagates, the core-shell particles rupture in a predetermined sequence and can introduce materials into the blast environment that act, for example, as a flame retardant and dispersant and suppressant, sound suppressant, smoke and dust suppressant. The core-shell particles can further introduce into the environment materials that are used to treat burns and other wounds, impede the dispersal of biological and radioactive agents, as well as RF shielding materials and materials which impede electrical impulse, designed to reduce the risk to first responders from a second detonation caused by other devices placed and planned to be triggered by a remote signal after their arrival to aid blast victims.

In other embodiments, fibers and textiles, in general, helmets, helmet liners or helmet liner pads, and any existing structure or item can be coated or provided with a film as illustrated, for example, in FIGS. 16, 17 and 22. Fibers can be woven into cloth and thereby shield the wearer at least partly from an impacting compression wave. The coated fiber 1600 of FIG. 16 includes a core fiber 1610 that has been coated with a sequence of mono-dispersed layers 1620 of particles with increasing size. The particles are confined through an intermediary material 1630. Alternatively, one could form a similar structure without the core fiber 1610 or remove the core fiber 1610 after the gradient layer structure has been formed.

In FIG. 17, an alternative coated fiber 1700 includes a core fiber 1710 that has been coated with the concentric composite material 1400 of FIG. 14. Different core-materials 1720 and 1730 for the composite material 1400 are indicated. A cloth including the coated fiber 1700 provides mitigation and/or remediation of an incident compression wave and additionally can provide agent materials, such as medicine or flame suppressants and retardants. Thus, agent materials can be introduced where they are needed the most upon impact of a bomb blast. Similarly, a helmet, helmet liner or helmet liner pads can be coated with composite materials of that kind as discussed in connection with FIG. 21. Alternatively, the helmet liner and helmet liner pads can be made with composite materials of the kind discussed in connection with FIG 21.

Destructive compression waves can also be generated under different conditions. For example, the opening and closing of valves in pipeline systems can generate compression waves, even shock waves that propagate along the pipes and can case damage, including the rupture of the walls of the pipes. FIG. 18 shows schematically a pipe 1800 with a valve 1830. To reduce the risk of compression wave induced damage, the inside of the pipe 1800 can be coated with a composite material 1810 including a gradient layer structure and an intermediary material 1815. The gradient can be formed perpendicular and/or parallel to the walls of the pipe 1800. A compression wave 1820 generated when operating the valve 1830 will then decrease in amplitude when impacting onto or traveling along the walls of the pipe 1800. Additionally, or alternatively core-shell particles can be included in the composite material 1810, thereby providing a core material for, e.g., mitigating the damage of leaking oil or sealing hair fractures of the pipe 1800. In addition, or alternatively, the outside can be coated similarly.

Thus, applications of the composite material can include the mitigation and/or remediation of a compression wave, caused by a bomb blast or the opening or closing of values, traveling along pipelines and other conduits used for transport of liquids and gases, to include fossil fuels, flammable liquids, and waste materials and to mitigate and/or remediate fire, leakage, release of gases and/or other effects. The composite material can be manufactured into a casing, outer and/or inner coating, cladding, film or liner. The composite material can further be designed to alleviate stress and fatigue caused by experiencing extreme changes in temperature.

In the following, the case of fossil fuel pipelines is discussed as a specific example in greater detail. Especially in areas with risk of asymmetric warfare, pipelines can be provided with layers of the composite material on the inside and on the outside. Then, the composite material can mitigate and/or remediate the effects of a bomb blast by absorption and dissipation in a predetermined manner, which can originate on either side of the material. In addition, one can use the wave to mitigate and/or remediate effects of the bomb blast and the leaking, eventually burning oil, by rupturing and/or vaporizing, e.g., core-shell particles, which populate specific layers within or next to the gradient layer structure of the composite material. Particles of the outside gradient layers, for example, can contain flame retardants and flame suppressants, foams and dispersants, smoke suppressants. Some core-shell particles can further include materials associated with the treatment of burns, infection, inflammation, pain, antibiotics, and materials used for triage medical treatment. Other core-shell particles can contain a material that blocks RF transmission, and impedes the dispersal of biological and/or radioactive agents.

The interior layers of the composite material are configured in a gradient layer structure to cause maximum disruption of compression wave and diminishing of the reflected wave. Some particles within or bordering to the gradient layer structure can be core-shell particles containing surfactants, which can break down and aid in the dispersal of fossil fuels in order to mitigate and/or remediate its effect on the environment. Inside and outside layers can contain core-shell particles with a core material that alleviates stress and fatigue caused by experiencing extreme changes in temperature.

When, for example, a bomb detonates next to the pipeline, the outer layers of the composite material closest to the detonation absorb the blast energy and cause thereby the rupture of the hollow particles and core-shell particles, which release their contents. As the shock wave moves through the composite material, deformation of the blast wave increases. Further, as the wave reaches those core-shell particle layers one after the other, the rupture of core-shell particles can occur in a predetermined sequence to provide a flame retardant and suppressant, generate non-flammable foam, and/or other coagulants designed to contain the flow of materials thereby preparing the area for decontamination and collection of the material released by the effect of the blast into the environment. Contemporaneously, the composite material can introduce into the blast's target environment the materials that treat burns and other wounds or impede the dispersal of biological and radioactive agents. It can further introduce into that environment RF shielding materials.

In FIG. 19, a hand held device 1900 is coated with a composite material 1910 to increase the resistance against impacts by affecting the propagation of a shock wave caused by, e.g., falling onto the ground. Alternative examples, for devices that can profit from shock absorption as explained, for example, in connection with FIG, 20 include laptops, cell phones, audio devices, and e-books.

FIG. 21 illustrates the application of the composite material in the context of a shielding device, specifically, a helmet 2100. The helmet includes a helmet structure 2110 to which helmet liner pads 2120 are attached. It is common to wear a helmet just with those helmet liner pads in certain environments. In addition, one can wear the helmet 2100 with a helmet liner 2130 that can give additional shelter for a specific environment (temperature, sun light, wind, sand, etc.). In some configurations, one uses the helmet liner 2130, for example, a cold weather helmet liner, with the helmet liner pads 2120. A compression wave caused by a detonating bomb or hitting a hard surface, e.g. pavement, can be mitigated and/or remediated based on a gradient layer structure and/or a core-shell material, which mitigate and/or remediate by absorption, dissipation, and providing core materials in a predetermined manner the effects of the compression wave striking the helmet 2100. The composite material can be incorporated into the helmet liner pads 2120 and/or the helmet liner 2130 and/or the helmet structure 2110.

The composite material, in addition to mitigating the effects of the compression wave, can signal concussive injury with or without penetration of the helmet 2100. It can provide immediate treatment of wounds with antibiotics, anti-inflammatories, pain medicine and blood coagulants, for example, for helmet penetrating and non-penetrating events before triage medical treatment. The composite material can therefore maximize the comfort of the helmet wearer while providing various safety features.

The composite material can be either applied directly onto the helmet as an inside and/or outside coating 2140. The composite material can further be incorporated in the helmet liner pads 2120 and/or the helmet liner 2130. Different composite material can also be provided in a series of pad elements 2121, 2122, 2123 thereby providing specific features at different locations. In some applications, the exterior layers of the pads closest to the wearer are designed to wick away moisture.

The material of the composite material can be self-extinguishing when exposed to combustion. The material can be a material that vaporizes and/or otherwise become a material, which will not drip, thereby protecting the scalp and skin of the wearer of the helmet 2100 from burns and aggravation of head and/or neck injury.

An exemplary structure for the series of pad elements 2121, 2122, 2123 is shown in FIG. 22. The microcapsules in each gradient layer rupture when impacted at different levels of force. The composite material that is closest to the scalp and skin and closest to the helmet structure is based on a gradient layer structure 2210, 2230. In FIG. 22, only one gradient layer structure is shown within the pad elements 2210 and 2230 but many more gradient layer structures with gradients of various directions can be used. The gradient layer structures 2210, 2230 each are sequenced to maximize the absorption of the compression wave.

The gradient layer structures of the pad elements 2210 and 2230 closest to the scalp and skin can further include core-shell particles 2240, 2250 with core materials such as flame retardants and suppressants, materials that wick away moisture, antibiotics, anti-inflammatories, pain medicine and blood coagulants.

The composite material of an intermediary pad element 2220 can include core-shell particles that provide after rupture an inelastic non-toxic inflammable foam. The foam can expand into a space 2150 between the head and the helmet structure 2110 thereby stabilizing the helmet head system and any head injuries. In addition, or alternatively, the foam can be contained within the helmet liner pad or pads and/or the helmet liner thereby increasing their size and tightening the helmet to the head. Thus, the inelastic foam mitigates and/or remediates by absorption and by keeping the helmet properly seated to protect the skull from further impacts and exposure to, e.g., the heat from combustion.

The helmet liner and/or the helmet liner pads can be made completely of pure composite material pad elements as shown in FIG. 22. Alternatively, a pad can include a cushioning material around which (or in between layers of the cushioning material) the composite material is wrapped in a textile like structure. For example, the intermediary pad element 2220 can be replaced with a cushioning material.

In some embodiments of the pads or the helmet liner, the composite material can include core-shell materials that contain a non-toxic, and washable, dye. Assuming that there is no penetration of the helmet 2100, when impacted by a compression wave, the gradient layer structures closest to the helmet mitigate and/or remediate the force of the compression wave. However, if the force of the impact is within a specified range, the composite material acts as a (physically triggered) sensor when the color filled core-shell particles rupture and mark the areas of impact or the occurrence of a compression wave.

When the helmet is removed, it is possible to determine that the wearer has sustained a possible concussive injury even though there is no penetration of the helmet. If the dye is triggered, after the helmet is examined, the dye can be washed out of the helmet.

The gradient layer structures continue to interact with following compression waves.

The layers closest to the skull, in addition to absorbing the impact, can also direct the force away from most sensitive areas of the skull thereby using the compression wave against itself to maximize the distortion of the compression wave.

Even in the case of a penetration of the helmet 2100, the core-shell particles closest to the skull, which can contain antibiotics and blood coagulants will rupture within the region of penetration, and thereby delivering their content into any wounds created and mitigating and/or remediating by triage treatment designed to stabilize medical conditions, prevent infection and to aid in cauterizing the wound.

The above discussed features can similarly be implemented in, e.g., different layers of a "cold weather" liner. Thus, the helmet liner 2130 itself can contain a composite material with core-shell particles providing various materials, when ruptured. In addition to absorb the blast wave, the generated foam can also protect against and treat neck wounds and provide acoustic protection as the foam can cover the neck and the ears of the wearer.

Due to the modular concept, the helmet liner pads 2120 and/or the helmet liner 2130 can be replaced after the mitigation and remediation of an impact or if some core-shell particles have ruptured or exchange is appropriate.

The above discussed features can similarly be implemented within the inside and/or outside coating 2140, which can be reapplied if necessary.

Example helmets include combat helmets and sport helmets, such as bike helmets, riding helmets, and motor cycle helmets.

The composite material can further be applied in form of a panel, e.g., a piece of molded composite material which you can attach to either a specific part, the door of a vehicle, for example, or which you can attach to a plate, like those suspended from the side of assault vehicles. The panel can further be easily transported and mounted to building or any object (large or small) that can benefit from shielding against compression waves.

In the following, the composite material is discussed in the context of shielding a transportation device, for military and/or civilian use. FIG. 23 shows schematically a transportation device 2300 such as vehicles, ships, boats, and aircraft, (airplanes, helicopters, space ships, etc.) or a part thereof. The transportation device can be manned or unmanned. It can transport people, surveillance devices, measurement devices, ordinance, or goods. Specific examples include tanks and Humvees (e.g., exterior shielding), airplanes, and helicopters (e.g., body, cockpit glass, engine, ordinance, and rotor blade shielding), unmanned drones used for surveillance and/or as a weapons platform (e.g., body, engine, optics, exterior and ordinance shielding), ships and submarines (e.g., hull and wall shielding).

The composite material can be applied to a surface of the transportation device 2300 as a coating 2310. Alternatively or additionally, the composite material can be attached to the surface as a removable unit 2320, e.g., as a film or panel that fits to and is shaped according to the shielded surface. Alternatively the composite material can be used as filling material for cavities of outer wall structures of the transportation device 2300, e.g., to fill the outer walls of ships or the doors of cars with, e.g., granular composite material based on concentric gradient layer structures.

The composite material mitigates and/or remediates the effects of a blast through its structure and by using that force as an activator to rupture and/or vaporize core-shell materials containing core materials, which are, e.g., flame retardants and suppressants, foam generators and dispersants, smoke suppressants, materials which can impede RF transmission and electrical impulses, materials associated with the treatment of burns, and other wounds, infection, inflammation, pain, antibiotics, and materials used for triage medical treatment,, and materials which act as a shield against biological and radioactive agents. The composite material can be transparent when applied, e.g., to glass, polycarbonate resin, or other materials used for viewing without essentially distorting visibility and degrading over period of use and exposure to extreme changes in temperature.

For example, for a vehicle, the composite material can be applied as a film attached to the surface of the vehicle, or can form completely molded panels attached to the sides, bottom and top. The composite material can be re-applied in field conditions after the composite material is triggered by a bomb blast. When used as a panel, as a coating, or as a film, the composite material can be light in weight. The outer layer of such a panel and/or film closest to the vehicle can contain a resin to bind it to the vehicle.

When, for example, a bomb detonates in the vicinity of the vehicle (representative for any transportation device), the outer layers of the composite material closest to the blast absorbs the blast energy causing the rupture of core-shell particles, the latter releasing the flame retardants, dispersants and suppressants, the smoke suppressants, as well as injecting into the targeted environment materials used to treat burns, and other wounds, infection, inflammation, pain, antibiotics, and materials used for triage medical treatment. Additionally, the composite material can introduce into that environment RF shielding materials or other materials to impede the transmission of electric impulses and thereby to reduce the risk to personnel already on site and to first responders from another bomb triggered by a remote signal following the initial blast. Materials to impede biological agents and radioactivity can also be introduced into the target area.

As the shock wave moves from the outer layer through the composite material, to the inner layer particles, deformation of the blast wave increases. Contemporaneously, the shock wave activates core-shell materials within the composite material, while at the same time the inner layers direct the shock wave in a predetermined manner to those areas where the vehicle is best protected against blast waves.

In FIG 24, a waste receptacle 2400 consists entirely of a composite material that includes gradient layer structures 2410 and 2415 and core-shell particles 2420 and 2430. The core-shell particles can be part of the gradient layer structure as illustrated for the core-shell particles 2420 in the gradient layer structure 2415. The core-shell particles can further form a layer themselves as illustrated for the core-shell particles 2430. The outer particles of the composite material can be confined by a binding layer 2440. The binding layer can include, for example, a sensor material that changes color in response to a chemical signature in its environment. The binding layer 2440 can alternatively or additionally be provided between layers of the composite material, e.g., between the core-shell particle layer 2430 and the gradient layer structure 2420.

Materials suitable as core material of the core-shell particles 2420, 2430, include flame retardants and suppressants, foam-generating materials and dispersants, materials which suppress and/or deform acoustic sound waves, materials which suppress smoke and dust, for example. The core material can further contain materials associated with the treatment of burns, and other wounds, infection, inflammation, pain, antibiotics, and materials used for triage medical treatment, Moreover, materials can include RF transmission blocking materials that impede electrical impulses, and/or materials, which impede the dispersal of biological and radioactive agents in order to reduce the risk to first responders from secondary devices placed and planned to be activated by remote signal. The core material can fill the shell completely or partly, and can be provided itself as core-shell particle(s), such as microcapsules.

One can manufacture the complex structure of the composite material for the waste receptacle layer by layer or attach pre-manufactured, e.g., layer sequences. The composite material can moreover be used in the form of a clear or opaque material.

As a shell material and/or a core material of the core-shall particle layers 2420 and 2430, the composite material can include a material that changes color (for example, in response to gaseous chemical signatures of explosives as discussed above in connection with FIG. 15), fire suppressant, and/or a rodenticide. For example, those materials can be present in the surface layer, or any inner layer of the composite material.

The structure as described in FIG. 24 can similarly also be the basis for a waste receptacle liner or any of the herein described embodiments. In general, any structure and use of material in any of the configuration described herein with reference to a specific application of the composite material can be applied in a similar way to another application or configuration of the composite material.

In the following, a large variety of materials are discussed that can be applied in the composite material, specifically, in the particles and core-shell particles. In general, the composite material can include particles of the same (single material system) or various different materials. In various embodiments, suitable particles can comprise silica; porous silica; aluminum hydroxide; polymeric materials; ceramic polycarbonate; metal and metal alloy spheres; perlite, carbonate; bicarbonate and halide salts; ceramics; silicates; chelators, such as, for example, calcium or EDTA; foams or foam generating reagents, or a combination thereof.

Fire suppression can be achieved with particles comprising one or more of potassium bicarbonate, aluminum, magnesium hydroxide, surfactants, aluminum hydroxide, potassium bicarbonate, halocarbons, potassium iodide, lithium carbonate, sodium carbonate, sodium hypochlorite, potassium nitrate, magnesium hydroxide and various other hydrates, fluorocarbon surfactants, hydrocarbon surfactants, hydroflurocarbons (HFCs), pentabromodiphenyl ether, antimony trioxide, halocarbons, chlorinated and brominated materials (polybrominated diphenyl ether (PBDE or DecaBDE, OCtaBDE, PentaBDE), polybrominated biphenyl (PBB) and brominated cyclohydrocarbons), and urethane.

For example, core materials that can be used for fire retardance or suppression include hydroxides and hydrates, halocarbons, carbonate, bicarbonate, halide and nitrate salts, polybrominated materials, surfactants and hydrofluorcarbons. In particular, aluminum hydroxide can break down under heat to provide two primary methods for extinguishing a fire ball associated with a bomb blast. First, it expels water vapor upon thermal breakdown which assists in quenching the fire. Additionally, the thermal breakdown process is endothermic and can thus absorb a large amount of heat resulting from the blast zone. Still further, the resultant material, after break down is an alumina (Al_2O_3), the presence of which can form a protective layer against the spread of fire. Still further, the inert gases produced (water and carbon dioxide) can also act as diluents in the combusting gas, effectively lowering the partial pressure of oxygen which slows the reaction rate.

In applications coupled with textiles, Tetrakis(hydroxymethyl) phosphonium salts can be used as core material

Moreover, ZrO_2 eruptively generated aerosol can serve as the anti-explosion and fireproof agent, and therefore, can be applied in security applications.

In some embodiments, Hydroflurocarbons (HFCs) can be used for fire suppression. In particular, a series of HFCs are commercially available from Dupont® that offer fire suppression with little or no ozone depletion. In some embodiments, pentabromodiphenyl ether can be used as a core fire retardant (eventually in conjunction with antimony trioxide). Still further, halocarbons can also be used as flame retardants core materials.

In some embodiments, chlorinated and brominated materials can also be used as fire retardant core materials. These materials can release hydrogen chloride and hydrogen bromide during thermal degradation. These react with H* and OH* radicals in the flame resulting in the formation of inert molecules and Cl* or Br* radicals. The halogen radicals have lower energy than H* and OH* and therefore reduce the propagation of the flame (reduction in oxidation potential). Antimony can also be used with halogenated flame retardants. Brominated flame retardants are produced synthetically in over 70 variants and are considered to be effective flame retardants. Any of the three classes of the brominated flame retardants can be separated into three classes or families: polybrominated diphenyl ether, polybrominated biphenyl, and brominated cyclohydrocarbons.

Fluorocarbon surfactants and hydrocarbon surfactants can also be used as flame retardants. For example, the fluorocarbon surfactants disclosed and described in U.S. patents 4,090,967 and 4,014,926, the entire disclosure of which are hereby incorporated by reference, can be used for coating gas lines and gas containing receptacles. These materials can produce foam that spreads over a surface, effectively suppressing the vaporization of gasoline. These foams can have, for example, an expansion ratio of between 50/1 to 1000/1. In order to mitigate and/or remediate a radioactive or "dirty" environment, potassium iodide can be used as a core material to mitigate and/or remediate, for example, radioactive iodine 131, which is known to cause thyroid cancer. Other core materials suitable for use in radioactive remediation include the known family of chelators. Chelators are materials that can selectively bind to radioactive metals. Two exemplary chelators commercially available in relatively large quantities are calcium and EDTA. In some embodiments, one or more particle layers of the composite material can comprise an inert material, such as, for example, a porous silica particle. To that end, porous silica can offer exceptional absorption characteristics.

Foam generating composite materials can be applied in applications such as petroleum/oil based conveyance systems, refining operations, chemical conveyance systems, and storage systems (e.g., as clotting or sealing material). As core-materials or particle materials, the foam generating composite material can then include, for example, epoxy materials (resin and hardener), which requires activation, an activating material, and a foaming agent. In addition, a reinforcing material, e.g., carbon fibers can be provided to be penetrated by the foam. Exemplary foaming agents include Telomer-based materials such as fluorosurfactants, aqueous film-forming foam (AFFF), alcohol-resistant aqueous film-forming foam (AR-AFFF), fluoroprotein (FP), film-forming fluoroprotein (FFFP), and alcohol-resistant film-forming fluoroprotein (AR-FFFP). Fluorosurfactants are based on perfluorinated telomer chemistry. Foaming agents can further include polyurethane, polyethylene, cross-linked, polystyrene, and urethane.

Composite materials for helmet liners or helmet liner pads can include, for example, latex based foam systems that require a latex solution as dissolved polymer, the foaming agent, a curative and a gel, as well as a fire retardant (e.g., one of the polybrominated class).

In some embodiment, the composite material can provide shielding against RF signals to assist in the prevention of a remote detonation. For example, an RF shielding layer can be provided by incorporating a conductive element in one or more of the particle layers. A number of materials are known to be capable of providing RF shielding, including, for example, copper and nickel. By incorporating electrically conductive and/or electromagnetic radiation absorptive particles into one or more layers, an RF signal can be shielded thus inhibiting the ability for remote detonation of an explosive device.

In some embodiments, one or more layers can comprise a piezoelectric material. According to this embodiment, the piezoelectric material can interact with vibrations of the surrounding environment to produce electricity. For example, acoustic waves could be used to attenuate a material designed as described so that piezoelectric materials in one of the layers are utilized to produce electricity. The produced electricity can then be harnessed for use internally by one or more layers of the composite material or can be used external to the material.

It should be understood that any one or more layers of the composite material can be customized to interact with or react to changes in the surrounding environment in a predetermined manner. To that end, the selection of materials depends on the particular predetermined interaction or reaction that is desired.

For selected core or agent materials, the microcapsules can be manufactured by conventional micro-encapsulation technique. Micro-encapsulation is defined as a process by which clusters of a solids, liquids or gases are packaged within a shell material. Micro-encapsulation is commonly distinguished as either a chemical or physical process. Both processes can be used to produce the core shell structures.

In some embodiments, the microcapsules can be formed from a conventional polymer or polycarbonate composition. It should be appreciated that such polymers and polycarbonates are further customizable in that they can be produced with a variety of physical attributes. For example, microcapsules can be manufactured having specifically desired strengths, elastic coefficients, colors, and thicknesses. The use of polymers can also offer energy absorbing characteristics as they decrease deflection of compression and sound waves. Further, polycarbonates can be used as a transparent material and ceramic/polycarbonate composite materials can be used, for example, in specific applications where increased levels of shielding (emf, induction, radiation etc.) are desired.

Exemplary chemical micro-encapsulation techniques that can be used to manufacture the encapsulated core-shell particles include polycondensation (interfacial polymerization), colloidosome formation, polymer precipitation by phase separation, layer-by-layer polyelectrolyte deposition, surface polymerization and copolymer vesicle formation. Likewise, exemplary physical micro encapsulation techniques include centrifugal extrusion, fluid bed, a Wurster process, and pan coating. In addition, centrifugal extrusion techniques can be used to produce larger particles, such as those ranging from about 250 micrometers to about a few millimeters in size.

In addition to the microencapsulated core-shell particles described above, one or more layers of the composite material can also comprise any of the core materials described above without the core or shell encapsulation coating. In addition, one or more layers can also comprise the microencapsulated shell coatings described above, in the absence of the core material.

The shell of a core-shell particle can be produced using a variety of processes. In various embodiments, the process used for the production of a core-shell particle can comprise FBE powder coating/lining; metallizing; electrostatic spray; dip coating; organic coating; parylene coating; spray coating; screen coating; roller, spin coating, extrusion processes, passive adsorption, covalent coupling, or any combinations thereof. In some embodiments, the process used for the production of a core-shell particle can comprise the one or more of the following techniques and/or material systems: polymers, for example, but not limited to baked phenolic, elastomeric urethane, epoxy, polyurethane, vinyl ester, polyester, polystyrene, or any combinations thereof.

It should be appreciated that any individual encapsulation method can be suitable for the production for particle sizes having a specific size range and that one or more methods can be suitable for the production of a specific size particle. Exemplary encapsulation methods and particle size ranges are detailed in Table 2 below. It should be appreciated that the recited ranges are not limiting and can vary.

Table 2

Encapsulation Method	**Size Range (μm)**
Physical Methods	
Stationary co-extrusion	1,000 - 6,000
Centrifugal co-extrusion	125 – 3,000
Submerged nozzle co-extrusion	700 – 8,000
Vibrating nozzle	> 150
Rotating disk	5 – 1,000
Pan Coating	> 500
Fluid bed	50 – 10,000
Spray drying	20 – 150
Chemical Methods	
Simple/Complex coacervation	1 – 500
Phase Separation	1 – 500
Interfacial polymerization	1 – 500
Solvent evaporation	1 – 500
In-situ polymerization	1 – 500
Liposome	0.1 – 1
Sol-gel methods	0.1 – 1
Nanoencapsulation	< 1

The multilayered composite material can be manufactured by a number of techniques. Initially, once the selection of particles and the corresponding particle sizes are determined for a given layer, these particles can be suspended in a liquid vehicle system or medium to form a batch composition for the given layer. The batch composition can then be used to form a layer of the material on a substrate. In one embodiment, it is contemplated that the succesive layers of the composite material can be applied as a film or coating to the substrate. Accordingly, a batch composition for each given layer can be provided and successivly applied to a surface of the substrate. Deposition techniques can include, for example, chemical vapor deposition, electrophoretic deposition, plasma enhanced vapor deposition, dip coating, sequential spray, foaming, spray coatings, casting, slurry based processes, and sequential processes. Those techniques can allow the production of waste receptacles and transparent liners.

In some embodiments, it is also contemplated that the composite material can be manufactured as a stand alone article without requiring it to be applied to or supported by a substrate. For example, sucessive batch compositions can be used to form multiple plys of a stand alone film. Alternatively, batch compositions can also be used to manufacture molded articles such as for example, injection molded, extrusion molded, and blow molded articles.

The batch composition for providing a given layer of the composite material can comprise a plurality of the desired particles suspended or dispersed in a suitable liquid vehicle system or medium. The liquid vehicle system can be formulated based upon any one of the following stabilization techniques including electrostatic stabilization, steric stabilization, electrosteric stabilization, depletion stabilization, stabilization by masking van der Waals forces, and stabilization by hydration forces. The stabilization mechanisms work by preventing or hindering the flocculation of the particles in suspension. In some embodiments, it is preferred for the liquid vehicle stabilization techniques to be an electrostatic or electrosteric stabilization. Electrostatic stabilization uses ions in solution to generate like charges on the particles in suspension. Electrosteric stabilization uses a charged polymer that adsorbs on the particle surfaces, causing double-layer repulsion. Either technique can be used to stabilize a suspension. Further, exemplary particles in liquid vehicle dispersions can be produced in aqueous form or from other suitable mediums that have low volatility and suitable thermal stability, such as for example, ethylene glycol.

For electrostatic stabilization, an acid or base (the choice of which can be dependant upon the charge of the particle surfaces) can be added to an aqueous suspension. The addition can adjust the pH of the suspension, which can affect the charge on the particle shear planes, *i.e.*, the zeta potential. If the particle surface has a positive charge, adding an acid to the suspension decreases viscosity effectively increasing the magnitude of the zeta-potential. When acid is added to the suspension, the particle shear planes develop a net negative charge, causing the particles to repel each other. The opposite is true for a suspension of negatively charged surfaces to which a base can be added to give the particle shear planes a net positive charge and in order to suitably disperse the particles in the suspension.

For electrosteric stabilization, the presence of a dispersant can directly influence the stability of the suspension until the particle surfaces are completely covered. Dispersants can be added in relation to the particles surface area, charge and size of the particles ensuring the correct amount of coverage. For example, in some embodiments, a polyelectrolyte dispersant should have the opposite charge of the particle surface being dispersed. The addition of a polyelectrolyte can change the isoelectric point allowing a dispersion to result without the need to adjust the pH of the suspension. When added to a suspension near the point of zero charge, the water used in the suspension can have a greater affinity for itself than the polymer, and hence the polymer can adhere to the particle surfaces. To prevent coagulation, an ionic solution can also be added to an electrosterically stabilized suspension to counter act the charge buildup. To that end, it should be understood that a stable suspension can be important as it can allow a higher solids loading with lower apparent viscosity than an unstable suspension can allow.

Still further, the batch compositions can comprise additives such as colorants, biocides, surfactants, plasticizers, binders, dispersants, acid, base, pore formers, and the like. Additionally, it should also be understood that the batch compositions can be formulated to provide transparent, translucent, or even opaque composite materials. For example, it can be desired for the composite material to be transparent. This can enable the manufacture of, for example, a transparatent film, liner or, alternatively, a composition that can be applied to glass or similar substrates without affecting the pre-existing transparancy of the substrate upon which it is applied. Alternatively, it can be preferred for the composite material to have a predetermined color suitable for use in forming stand alone articles or coatings having certain aesthitic appearances.

As summarized above, it is further contemplated that the composite materials can be used in a variety end use applications including, for example, military, energy and related infrastructure, electronics, sensors and actuators, lubricants, medical applications, catalysis, structural materials, ceramics, civil engineering applications, aerospace, automotive applications, textile and antiballistic materials. In some embodiments, it is contemplated that the composite material is particularly well suited for use as or in combination with an antiballistic material.

In some embodiment, a composite material can be applied onto the surface of any desired object in order to provide the blast energy absorption and any secondary blast mitigation effects described herein. For example, the material can be applied to the inside surface of a trash receptacle. Alternatively, the material can be provided in the form of a stand alone film that is suitable for use in manufactuing liners that can be removably placed inside pre-existing trash receptacles. The liner can be manufactured having any predetermined color. Alternatively or in addition, the liner can also be transparent. Still further, it is also contemplated that the composite material can be used to form the trash receptacle itself thus eliminating the need to apply either a separate coating or a liner in order to provide the blast energy absorption and any secondary blast mitigation effects described herein. Once again, the manufactured trash receptacle can also have any predetermined color or be transparent.

Thus, the response of the composite material can be considered to be smart in that it does have a designed or engineered response to an external stimulus. Specifically, the properties of the composite material adapt in response to the external stimulus. The composite material can be further provided to be multifunctional, e.g., include multiple features such as absorption of compression waves, mitigation of fire, remediation of biological systems etc.

EXAMPLES

The invention is further described in the following examples, which do not limit the scope of the invention described in the claims.

Prophetic example 1: Exemplary batch composition

In an exemplary embodiment, a composite material could be comprised of a plurality of tape casted layers. The tape casting could be used to apply the composite material layers to a pre-existing substrate or to form a stand alone multi-layered composite material. An exemplary and non-limiting batch composition that could be used to prepare each successive layer of the composite material is set forth below in Table 3:

Table 3

Component	wt%	Function
Microspheres	55.66	Layer 1
Xylene	18.55	Solvent
Ethanol	18.55	Solvent
Butvar 98[1]	4.08	Binder
Menhaden oil	1.12	Dispersant
Santicizer 160[2]	1.02	Plasticizer
UCON[3]	1.02	Plasticizer

[1] Commercially available from Electron Microscopy Sciences, Hatfield, Pennsylvania;
[2] Commercially available from the Ferro Corporation, Walton Hills, Ohio;
[3] Commercially available from Dow Chemicals, Midland Michigan

Based upon the formulation set forth in Table 3, the microspheres, solvents and dispersant can first be mixed in a ball-mill for approximately 24 hours. After mixing in the ball mill, the binder and plasticizer component can then be added to the ball mill and the resulting mixture can be mixed for another 24 hour period. After mixing is completed, the composition can be tape cast onto a coated paper or a steel belt to form a particle layer. The tape casting can be performed by using a commercially available tape casting apparatus such as a Unicast 2000. The tape cast layer can then be allowed to dry naturally under ambient conditions. This process can be repeated using batch compositions comprised of particles having differing median particle sizes until a desired number of particle layers have been tape cast to form the particle size gradients described herein.

Prophetic example 2: Use as a blast wave absorbing material

With reference to FIG. 1, the material of the composite material can be used as a blast wave absorbing material. For example, a material manufactured according to prophetic example 1 can be disposed on the interior surface of a waste receptacle so that the layer 110 comprising the largest median particle size is oriented to be the first layer exposed to the impact of the bomb blast shock wave. The layers comprised of smallest particles, layer 170, would be position or located adjacent to the waste receptacle wall. The layers 110, 120, and 130 can be comprised of particles having the core-shell microstructure as depicted in FIG. 11. The shell 1120 of the material can be pliable such that it can deform upon impact of a bomb blast (shock wave 20). The particle cores can be comprised of one or more blast mitigating materials, such as sodium hypochlorite, potassium nitrate, and the like. Layer 140 can comprise a RF shielding material (such as copper, nickel, copper and nickel alloys, cermets, and the like). The adjacent remaining layers 150, 160 and 170 can be comprised of particulate materials, such as a porous silica, whose median particle size distribution allows a sufficient increase in the inter layer particle contact points to efficiently reduce the impact 105 across the material 100 and the remaining layers (150, 160 and 170).

Upon impact of the shock wave 20, the core-shells in layers 110, 120 and 130 can deform and a portion of the energy associated with the bomb blast can be removed from the system due to this deformation. As the shells deform, they can also apply pressure to the adjacent particles upon which they contact, thus, transferring impact energy to the energy required for deformation and angular pressure on its neighboring particles. Ultimately the shells 1120 deform to a point where shell rupture occurs releasing the core fire retardant materials directly into the blast zone. As the core-shell particles rupture in successive layers, the cores from different particles are introduced into the blast zone, which can further enable, if desired, more complex systems or combinations of systems to be introduced, thus allowing sequential reactions to occur in a user defined manner. The staggering of core materials in a pre-designed manner allows sequential reactions whose sum reaction is greater than their individual contributions.

In addition to the core-shell rupturing, as the shock wave 20 traverses across the first layer 110, it would reach the interface between the first layer 110 and the second layer 120. As the particles comprising the first layer 110 are larger than the particles populating the second layer 120, there also exists at the interface an increase in surface contact points. As in the case of the first layer 110, the impact energy, deforms, compresses and re-orientates the individual particles comprising the second layer 120 resulting in a reduction of the energy of the impact 105. The deformation, compression, re-orientation and transfer of energy relationships continues across the cross section of the material 100 and though subsequent layers from layers 120 to 130, 130 to 140, 140 to 150, 150 to 160 and 160 to 170.

Prophetic example 3: Experimental Design

In some embodiments, a composite material could be comprised of encapsulated materials having particle sizes of 500 nm, 5 μm, and 50 μm. The mean particle diameter and the tensile strength of a particulate filled rigid polyurethane resin at a given volume fraction can be expressed as a linear relationship. In addition, the ability of the particle to flow and compress decreases with average particle size, while strength and transverse rupture strength (TRS) increase with decreasing particle size.

A unique slope of the linear relationship between friction angle and void ration was identified for monosize specimens of varying particle shapes. It was also observed that the friction angle decreases as the aspect ratio increases provided that the void ratio of the two specimens was the same. The friction angle was proportional to the coordination number for monosize specimens regardless of individual specimen size.

Testing protocols for a composite material produced in accordance with the present invention can include: 1) shock tube analysis wherein shock waves are generated by the rupture of a thin diagram separating high and low pressure gases, wherein samples are mounted at the end of a tube; 2) simulations of blast effects using small (e.g., gram range) explosive charges, scaling models, and optical shock wave imaging techniques, wherein shock waves are simulated using scaling law; and 3) detonation techniques wherein the velocity at which a detonation wave travels through the explosive product is determined, typically in the range of from about 2,000 to about 8,000 m/s.

It should be appreciated that several types of experimental designs can be investigated. For example, experimental designs based upon particles can be investigated. The primary input of energy occurs via the interaction of clusters, molecules, atoms, or ions with a surface. The amount of transferred energy ranges from eV to a few keV. Energy dissipation processes can be studied by means of spectroscopic techniques and laser interferometry. These experiments are not time resolved, but rather quasi-stationary. Dynamics can also be investigated. For example, a dynamic observation can be made of the energy dissipation process requiring excitation of a surface via an ultra-short laser pulse providing photon energies of a few eV. Using a pump-probe technique with a second delayed pulse can probe the reaction of a system upon excitation. Analysis techniques can include diffraction, spectroscopic techniques, laser interferometry, and various imaging techniques. Still further, effects of friction can also be investigated. This can include a study of the transport of particles and electrons at surfaces and in thin layers, particularly energy dissipation due to both mechanical friction and friction due to scattering at the surface and interfaces. Friction analysis techniques can include spectroscopic and imaging techniques.

Production of materials, such as, for example, core-shell particles, can comprise a solvent case process, a continuous solvent cast process, an extrusion process, and a combination thereof. In some embodiment, such a process can require that the material and/or precursor materials be at least partially soluble in a volatile solvent or water; remain stable in solution with a reasonable minimum solid content and viscosity; and be capable of forming a homogeneous film and/or an in-situ gradient, and releasing from a casting support.

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A multilayer composite material, comprising:

   a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient.

2. The multilayer composite material of claim 1, wherein the gradient layer structure is configured such that a change in particle size between neighboring layers ranges from 5% to 50% of the mean particle size.

3. The multilayer composite material of claim 1, wherein a largest particle layer is positioned towards an impact side of the multilayer composite material of a compression wave, thereby providing a decreasing size of particles in direction of a propagating compression wave.

4. The multilayer composite material of claim 1, wherein a smallest particle layer is positioned towards an impact side of the multilayer composite material of a compression wave, thereby providing an increasing size of particles in direction of a propagating compression wave.

5. The multilayer composite material of claim 1, wherein a number of contact points per area between particles within neighboring layers changes according to the particle size gradient.

6. The multilayer composite material of claim 1, wherein the thickness of at least one of the layers is about the mean particle size of that layer.

7. The multilayer composite material of claim 1, wherein particles within at least one of the layers and/or between neighboring layers are in contact with each other.

8. The multilayer composite material of claim 1, wherein particles within at least one of the layers and/or between neighboring layers are positioned with respect to each other such that the particles get into contact during the impact of a compression wave.

9. The multilayer composite material of claim 1, wherein the particles are configured for unrestrained interaction between particles.

10. The multilayer composite material of claim 1, wherein the particles include at least one of solid particles, hollow particles, core-shell-particles, microspheres, and spherical particles.

11. The multilayer composite material of claim 1, wherein the gradient layer structure includes at least one layer with a particle size smaller than 1mm, 0.1 mm, 0.04 mm, 1000 nm, 500 nm, 100 nm, or 10 nm.

12. The multilayer composite material of claim 1, wherein the gradient layer structure includes at least one layer with a mean deviation below about 10 % for a median particle size distribution.

13. The multilayer composite material of claim 1, wherein the particles are dispersed in a resin that allows momentum transfer to neighboring particles.

14. The multilayer composite material of claim 1, wherein the gradient layer structure includes a pore microstructure and the pore microstructure is at least partially filled with air, gas or an intermediary material.

15. The multilayer composite material of claim 1, wherein the gradient layer structure is a first gradient layer structure having a first particle size gradient in a first direction and the composite material further comprises a second gradient layer structure having a second particle size gradient.

16. The multilayer composite material of claim 1, further comprising a substrate and the gradient layer structure is applied to the substrate.

17. The multilayer composite material of claim 1, wherein the multilayer composite material is configured as a self supporting structure.

18. The multilayer composite material of claim 1, wherein the gradient layer structure is a concentric gradient layer structure around a center particle.

19. The multilayer composite material of claim 18, wherein the center particle is a core-shell particle.

20. The multilayer composite material of claim 18, wherein multiple concentric gradient layer structures are configured as a coating applied to a substrate.

21. The multilayer composite material of claim 18, wherein multiple concentric gradient layer structures are configured as a self supporting article.

22. The multilayer composite material of claim 1, wherein the gradient layer structure is configured such that a compression wave propagating in the gradient layer structure is distorted.

23. The multilayer composite material of claim 1, further comprising a core-shell particle layer of core-shell particles having a shell surrounding a core material.

24. The multilayer composite material of claim 1, wherein the gradient layer structure comprises a core-shell particle layer of core-shell particles having a shell surrounding a core material.

25. The multilayer composite material of claim 1, wherein at least one particle contains a polymeric material selected from a group consisting of urethanes, vinyls, epoxies, phenolics, styrenes, and esters.

26. The multilayer composite material of claim 1, wherein at least one particle contains a fire suppressant selected from a group consisting of carbonate, bicarbonate or halide salts, telomer based materials that incorporate fluorinated materials, halocarbons, hydrofluorocarbons, hydroxides, hydrates, and polybrominated materials.

27. The multilayer composite material of claim 1, wherein at least one particle contains an agent material for generating a foam.

28. The multilayer composite material of claim 1, wherein at least one particle contains a medical active material selected from a group consisting of antibiotics, medicines to treat infections, disinfectants, pain medication, anti-inflammatories, burn relief agents, and biological/radioactive remediative materials.

29. The multilayer composite material of claim 1, wherein at least one particle is a core-shell material and a material of the core, when released, is selected to react with at least one of another core material, a shell material, an intermediary material, and the material of neighboring particles.

30. The multilayer composite material of claim 1, wherein the material of particles of at least one of the layers is an RF shielding material.

31. A composite material, comprising:

a core-shell particle layer of core-shell particles having a shell surrounding a core material and the shells being in contact with each other or close to contacting each other and being configured to release the core material when impacted by a compression wave through momentum transfer from the compression wave onto the shell.

32. The composite material of claim 31, wherein at least one of the core-shell particles includes a shell material containing a polymeric material selected from a group consisting of urethanes, vinyls, epoxies, phenolics, styrenes, and esters.

33. The composite material of claim 31, wherein at least one of the core-shell particles includes a core material containing a fire suppressant selected from a group consisting of carbonate, bicarbonate or halide salts, telomer based materials that incorporate fluorinated materials, halocarbons, hydrofluorocarbons, hydroxides, hydrates, and polybrominated materials.

34. The composite material of claim 31, wherein at least one of the core-shell particles includes a core material containing an agent material for generating a foam.

35. The composite material of claim 31, wherein at least one of the core-shell particles includes a core material containing a medical active material selected from a group consisting of antibiotics, medicines to treat infections, disinfectants, pain medication, anti-inflammatories, burn relief agents, and biological/radioactive remediative materials.

36. The composite material of claim 31, wherein at least one of the core-shell particles includes a core containing a material, when released, to react with at least one of another core material, a shell material, an intermediary material, and the material of neighboring particles.

37. The composite material of claim 31, wherein at least one of the core-shell particles includes a core containing a material configured, when released, to mitigate a secondary effect of an explosion.

38. A multilayer composite material, comprising:

a gradient layer structure including a sequence of layers of microscale particles and at least one layer of core-shell particles, wherein a shell of at least one of the core-shell particles is configured to release a core material of the core-shell particle under a threshold physical condition that is controlled by a gradient of the gradient layer structure.

39. The multilayer composite material of claim 38, wherein the position of the core-shell particle layer in the gradient layer structure defines a minimum pressure of an impacting compression wave that is required to initiate the release of the core material.

40. The multilayer composite material of claim 38, wherein the gradient layer structure is configured to reduce a compression wave to provide a predefined threshold pressure at the core-shell particle layer.

41. A method, comprising:

absorbing energy of a compression wave with a gradient layer structure of microscale particles, at least one of which being a core-shell particle; and using the absorbed energy to release a core material from the core-shell particle.

42. A liner, comprising:

a composite material including at least one of

a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, and

a core-shell particle layer of core-shell particles having a shell surrounding a core material.

43. The liner of claim 42, wherein the liner is transparent, opaque, or non-transparent.

44. A receptacle, comprising:

a composite material including at least one of

a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, and

a core-shell particle layer of core-shell particles having a shell surrounding a core material.

45. The receptacle of claim 44, wherein the receptacle is transparent, opaque, or non-transparent.

46. A system, comprising:

a pipe; and

a composite material including

at least one of a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, and

a core-shell particle layer of core-shell particles having a shell surrounding a core material,

wherein the composite material is applied to at least one of the inside surface and the outside surface of the pipe.

47. A helmet liner pad comprising:

a composite material including at least one of

a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, and

a core-shell particle layer of core-shell particles having a shell surrounding a core material.

48. The helmet liner pad of claim 47, wherein the composite material includes a polymer layer and a binding layer that at least partly surrounds the polymer layer.

49. The helmet liner pad of claim 47, further comprising an attaching structure at one side of the helmet liner pad for attaching the helmet liner pad to a helmet.

50. A textile, comprising:

a cloth; and

a composite material including at least one of

a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, and

a core-shell particle layer of core-shell particles having a shell surrounding a core material,

wherein the composite material is applied to the cloth.

51. A transportation device, comprising:

a body; and

a composite material including at least one of

a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, and

a core-shell particle layer of core-shell particles having a shell surrounding a core material,

wherein the composite material is applied to the body.

52. The transportation device of claim 51, wherein the gradient layer structure is configured as one of a coating, a film, and a panel.

53. The transportation device of claim 51, wherein the gradient layer structure is provided within a cavity of a structural component of the transportation device.

54. A composite material comprising at least one of

a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, and

a core-shell particle layer of core-shell particles having a shell surrounding a core material,

wherein the composite material includes a color changing sensor material.

55. The composite material of claim 54, wherein the color changing sensor material is configured to change color when exposed to at least one of a gaseous explosive material, vapor of an explosive material, a chemical material outgased from an explosive material, and chemical components of an explosive material.

56. The composite material of claim 54, wherein the color changing sensor material is configured to change color when exposed to a compression wave.

57. The composite material of claim 54, wherein the color changing sensor material is contained in at least one of the microscale particles, the core-shell particles, an intermediary material, a material of a binding layer, and a material of a binding film of the composite material.

58. A helmet, comprising:

a helmet structure; and

a composite material including at least one of

a gradient layer structure of a sequence of layers of microscale particles, wherein a mean particle size of particles of neighboring layers varies from layer to layer, thereby forming a particle size gradient, and a core-shell particle layer of core-shell particles having a shell surrounding a core material,

wherein the composite material is applied to the helmet structure.

FIG. 1

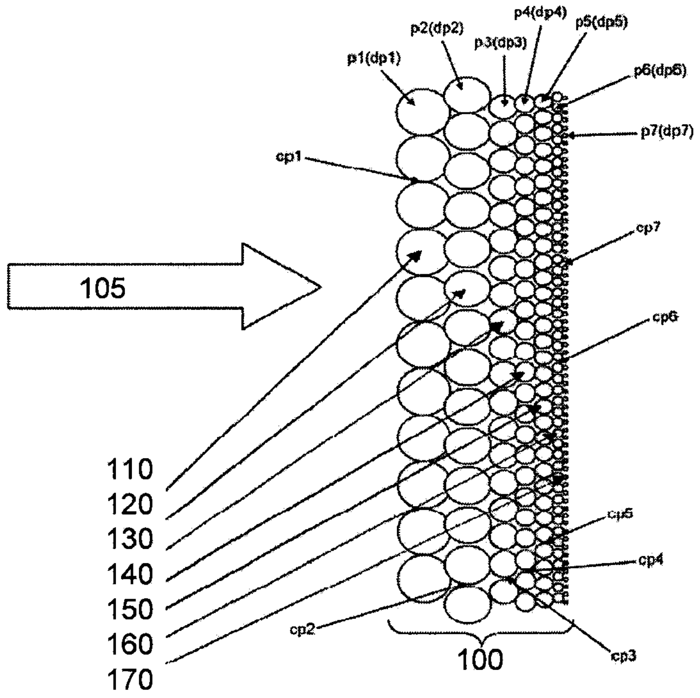
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FIG. 2

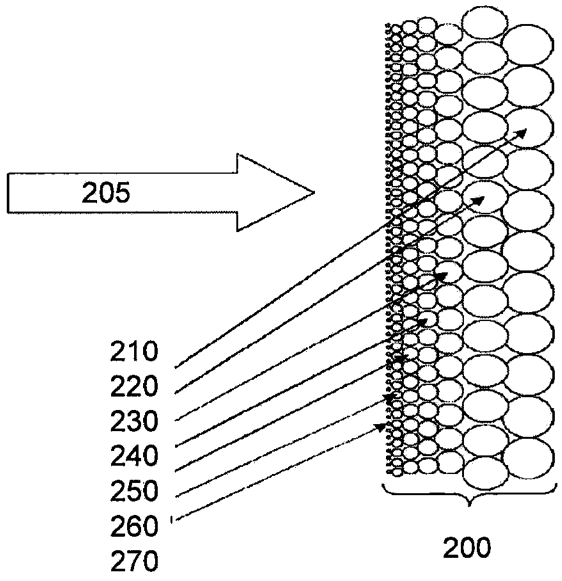
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FIG. 4

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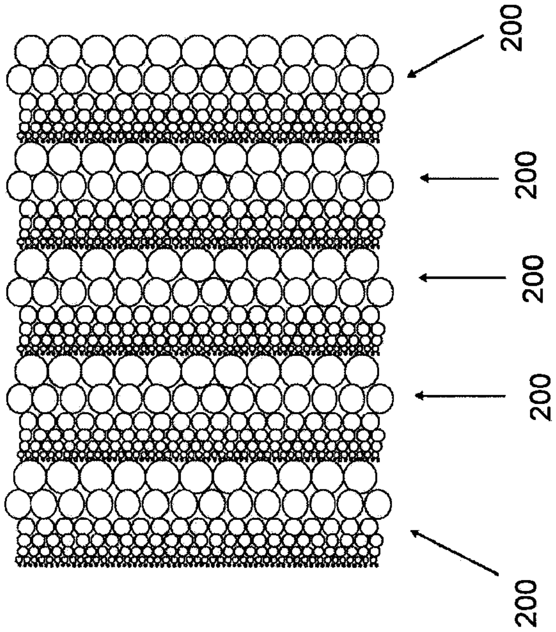

FIG. 3

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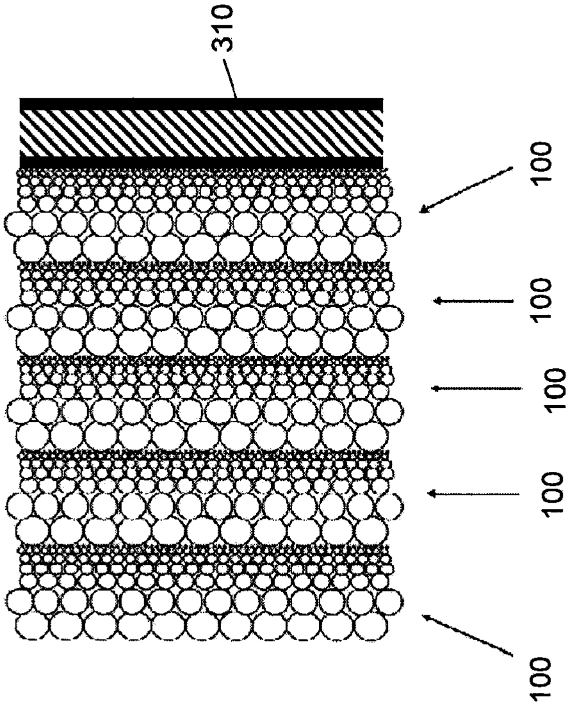

FIG. 5

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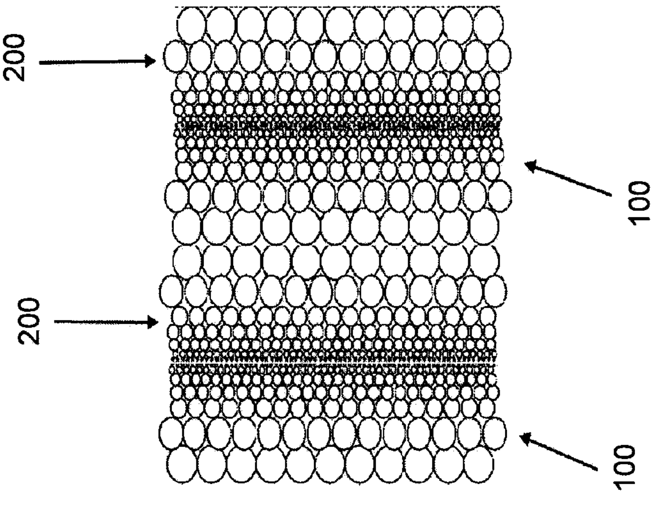

FIG. 6

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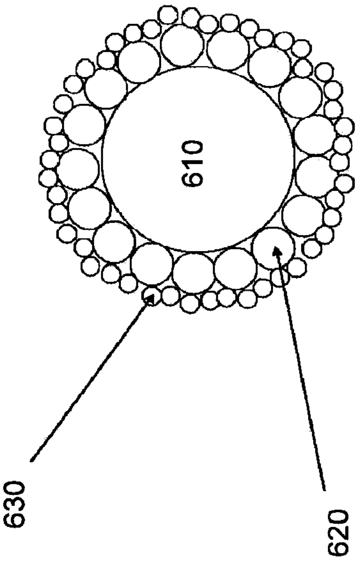


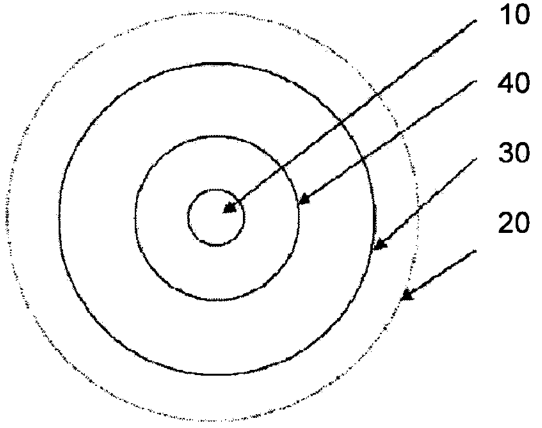


FIG. 7

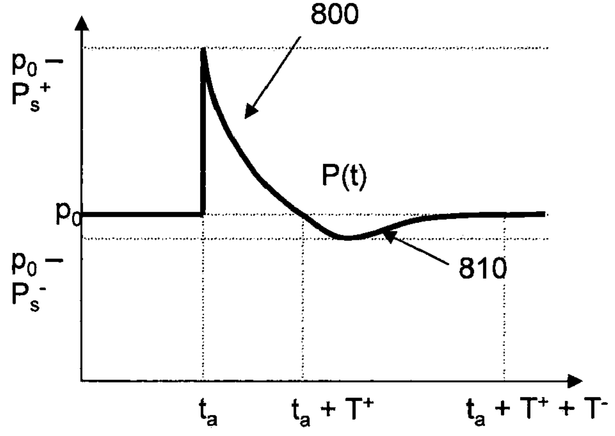


FIG. 8

FIG. 9

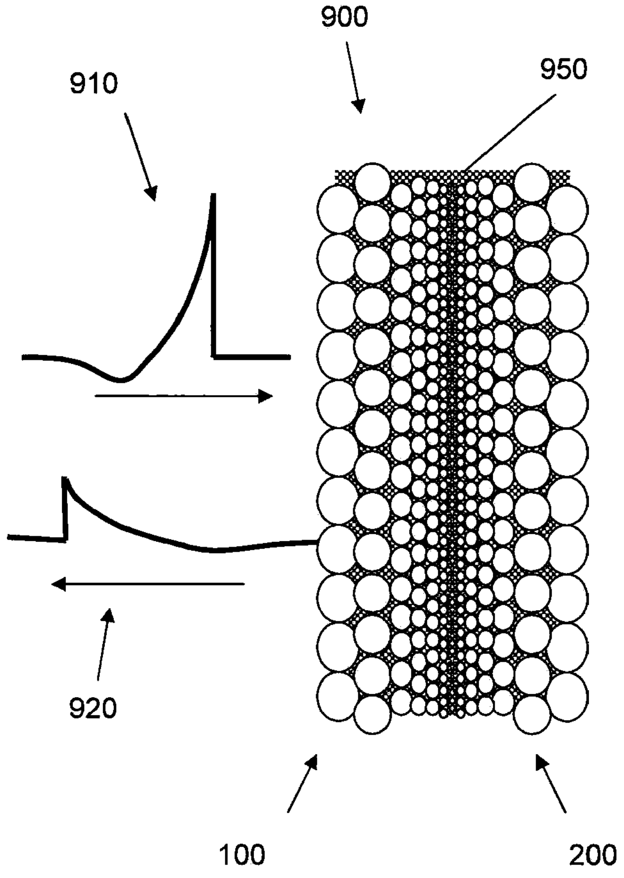


FIG. 10

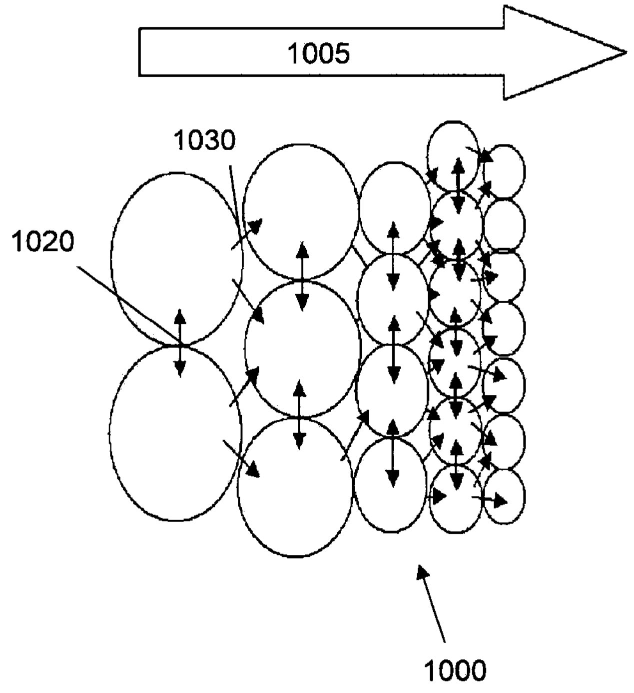


FIG. 11

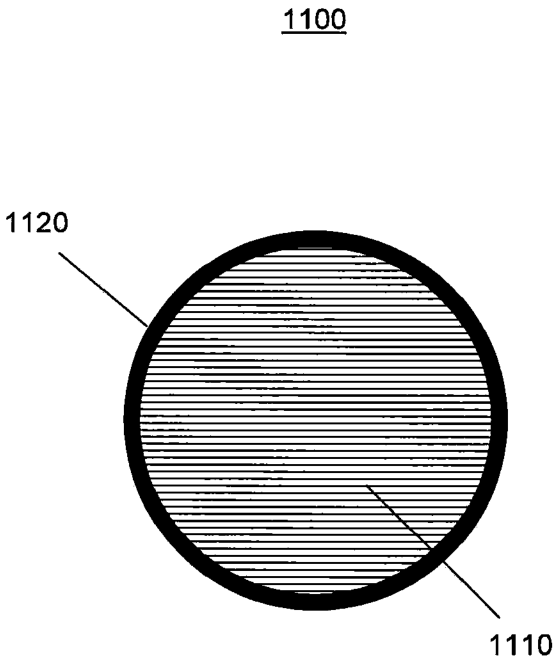


FIG. 12

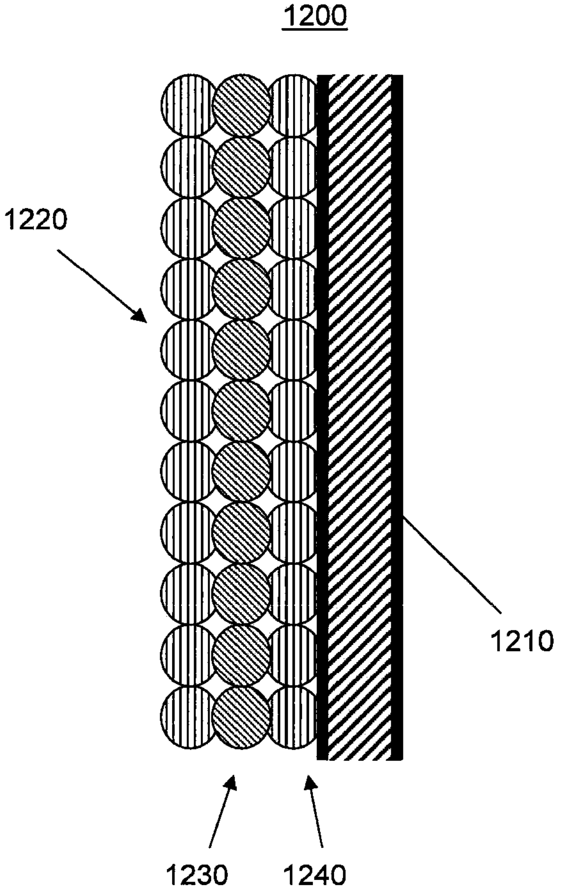


FIG. 13

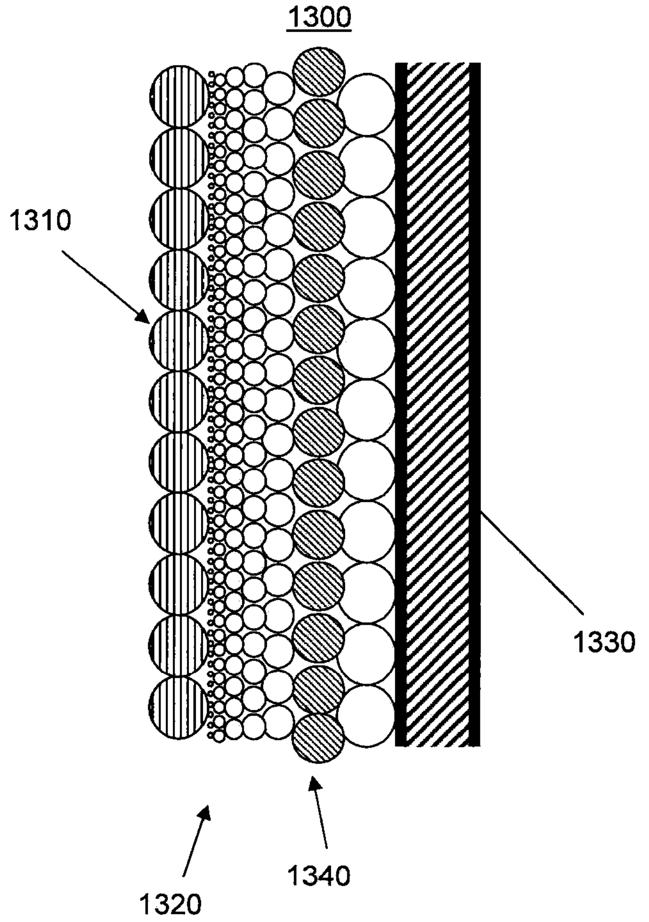


FIG. 14

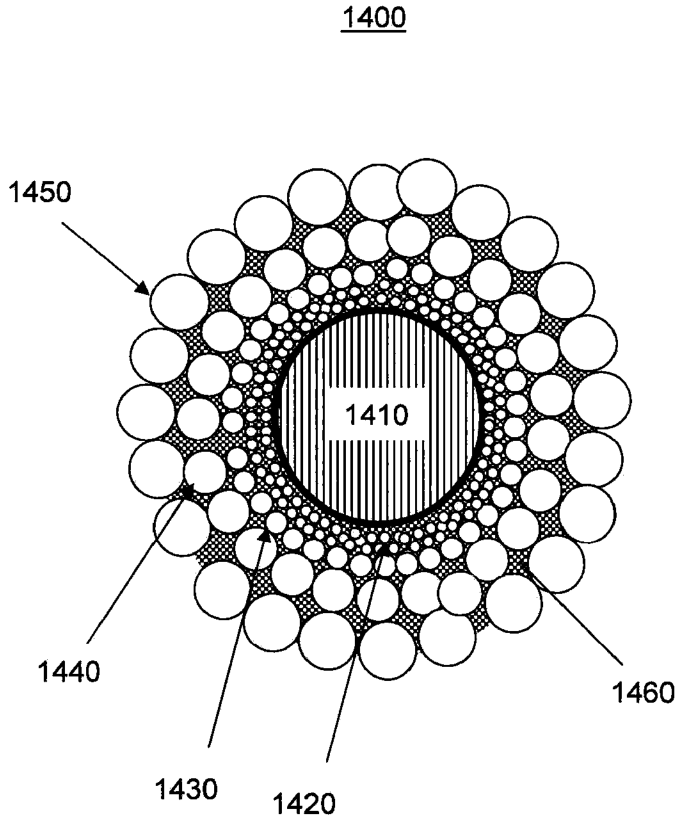


FIG. 17

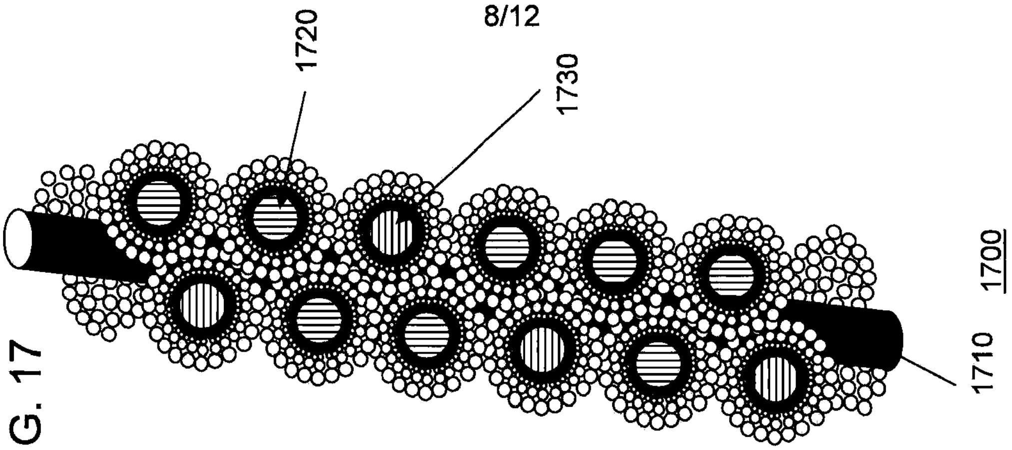


FIG. 16

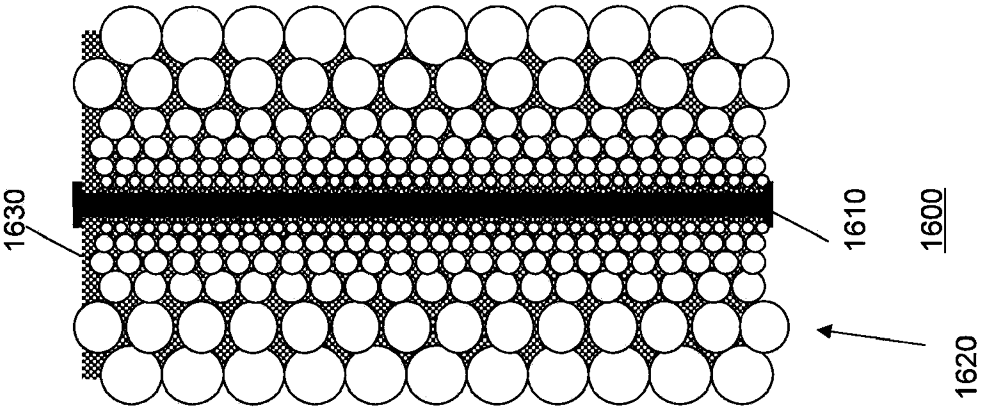
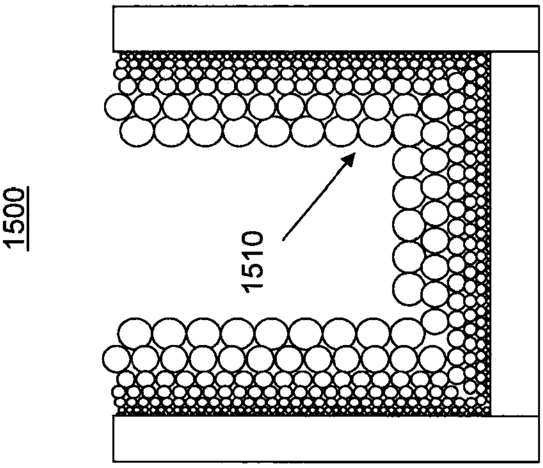


FIG. 15



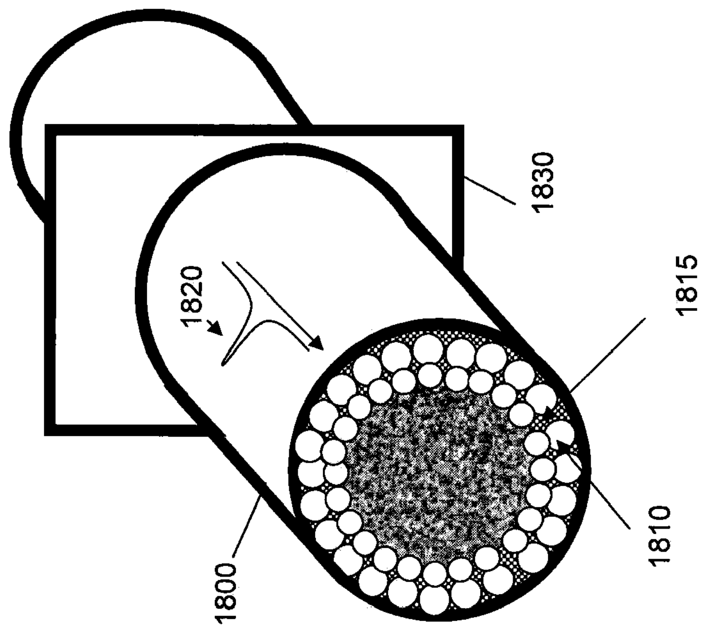


FIG. 18

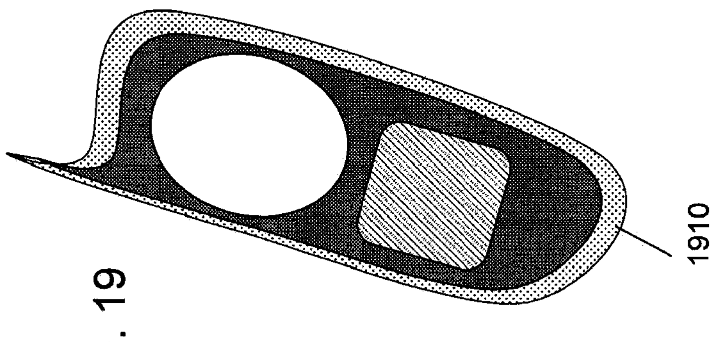


FIG. 19

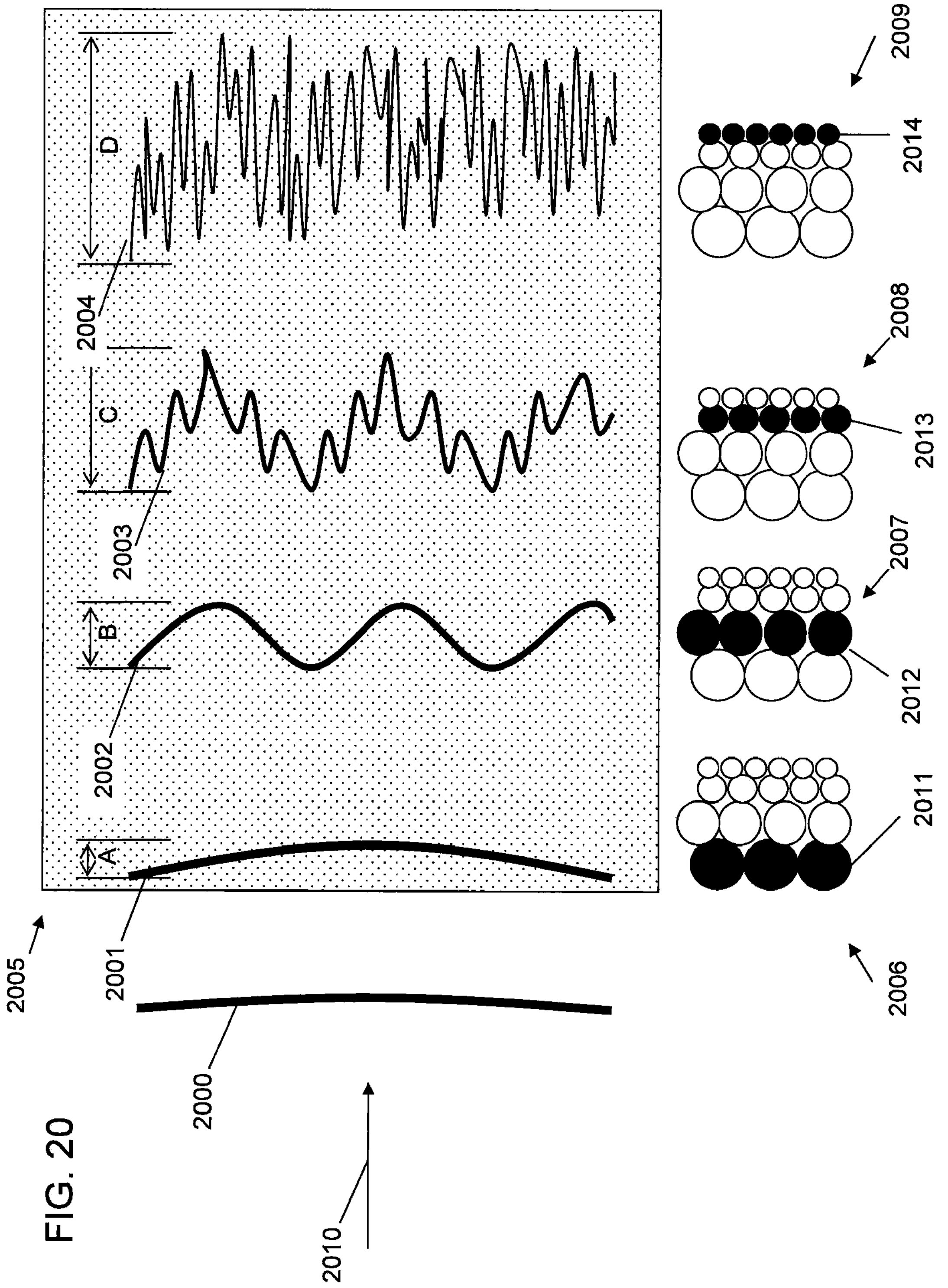

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FIG. 20

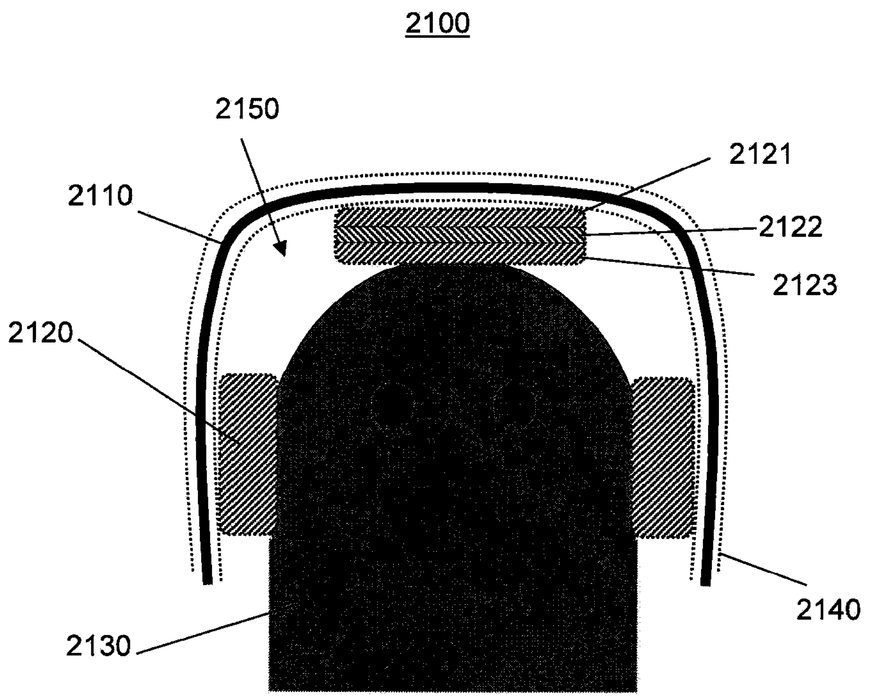
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FIG. 21

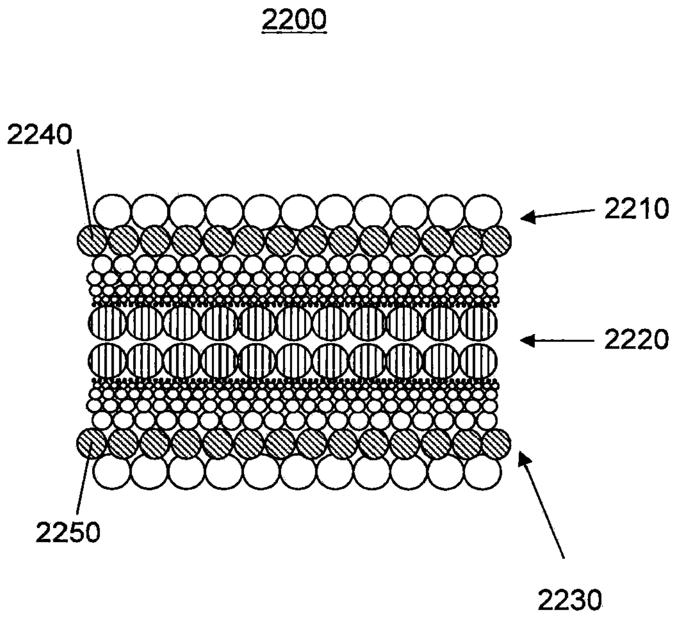
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FIG. 22

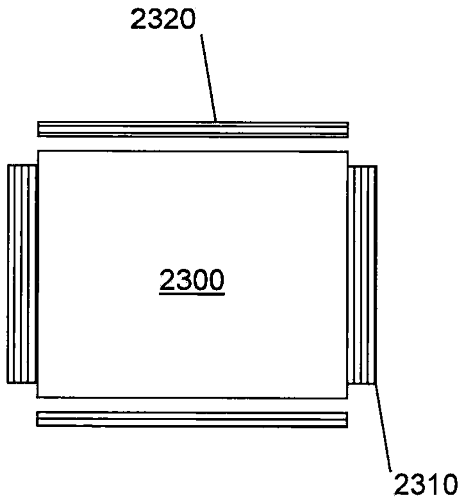

FIG. 23

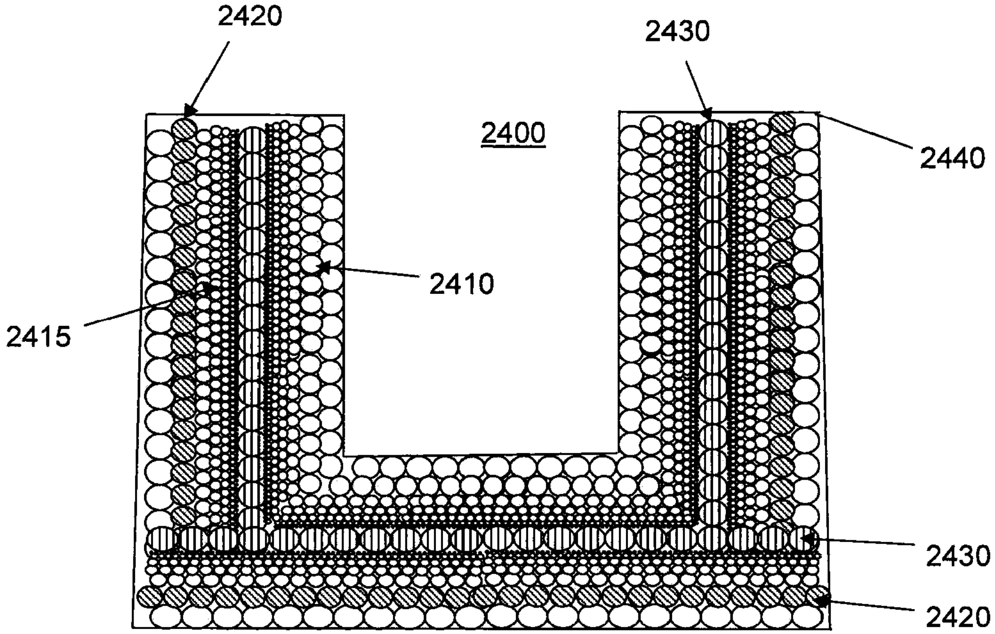

FIG. 24