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European patent

It is hereby certified that a European patent has been granted in respect of the invention described in the patent specification for the Contracting States designated in the specification.

CERTIFICAT

Brevet européen

Il est certifié qu'un brevet européen a été délivré pour l'invention décrite dans le fascicule de brevet, pour les Etats contractants désignés dans le fascicule de brevet.

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(54) FLEXIBLE HIGHLY FILLED COMPOSITION, RESULTING PROTECTIVE GARMENT, AND METHODS OF MAKING THE SAME

FLEXIBLE HOCHGEFÜLLTE ZUSAMMENSETZUNG, SCHUTZKLEIDUNG DARAUS UND VERFAHREN ZUR HERSTELLUNG DAVON

COMPOSITION FLEXIBLE HAUTEMENT CHARGÉE, VÊTEMENT PROTECTEUR AINSI OBTENU ET PROCÉDÉS DE FABRICATION DE CELLE-CI

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Description

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Application No. 14/068,297, filed October 31, 2013, which claims the benefit of U.S. Provisional Application No. 61/720,553, filed October 31, 2012.

FIELD

[0002] The present disclosure relates to polymer composition and protective garments. More particularly, the disclosed subject relates to filled polymer compositions, resulting protective garments for radiation protection, and methods of making the same.

BACKGROUND

[0003] Protective garments and related equipment are designed to protect a user's body from harm or injury caused by hazards such as radiation. Ionizing radiation is widely used in industry, medicine and laboratory, and it presents a significant health hazard. Radiation blocking garments can shield a user's body and block radiation. For example, X-ray blocking garments are worn by people exposed to non-enclosed (open) X-ray beams having energies between 60 and 120 kV. In addition to efficiency in blocking radiation, it is desirable for radiation blocking garments to have good mechanical properties and chemical resistance.

SUMMARY OF THE INVENTION

[0004] The present disclosure provides a filled composition as set out in claim 1 for blocking radiation such as X-ray, a resulting sheet as set out in claim 14 comprising such a filled composition, a resulting protective garment as set out in claim 15 comprising such a filled composition, and the methods of making the same.

[0005] In some embodiments, the filled composition comprises at least one polymer ingredient and at least one metal-containing filler. The at least one polymer ingredient is selected from the group consisting of a polyolefin elastomer, a polyolefin co-polymer, a polyolefin ter-polymer, and a combination thereof. The polyolefin elastomer, the polyolefin co-polymer, or the polyolefin ter-polymer comprises monomer units derived from ethylene and at least one vinyl monomer having more than three carbon atoms, for example, from four to ten carbon atoms. The at least one metal-containing filler is selected from a metal filler, a metal compound and a combination thereof.

[0006] In some embodiments, the at least one polymer ingredient comprises a polyolefin elastomer (POE). The POE, for example, can be a copolymer of ethylene and at least one vinyl monomer selected from the group consisting of butene, pentene, hexene, heptene, octene and a combination thereof. In some embodiments, the at least one polymer ingredient comprises a polyolefin elastomer (POE) comprising a copolymer of ethylene and octene.

[0007] In some embodiments, the at least one polymer ingredient comprises an olefin block copolymer (OBC) having alternating blocks of rigid and elastomeric segments. The OBC can be a copolymer of ethylene and at least one vinyl monomer selected from the group consisting of butene, pentene, hexene, heptene, octene and a combination thereof. For example, an OBC can be a copolymer of ethylene and octene.

[0008] In some embodiments, the at least one polymer ingredient further comprises an ethylene-vinyl acetate copolymer, an ethylene-propylene-diene (EPDM) ter-polymer, or a combination thereof.

[0009] According to the invention the at least one metal-containing filler comprises a metal having an atomic number greater than 50. For example, the at least one metal-containing filler comprises Sb, W, Ba, Pb, Bi, an alloy thereof, an oxide thereof, a salt thereof, or a combination thereof. In some embodiments, the at least one metal-containing filler can be substantially free of Pb, and comprises a filler selected from Sb, W, Bi, $BaSO_4$, and a combination thereof.

[0010] The filled composition can further comprise an additive package, which comprises an additive selected from the group consisting of a paraffinic oil, an aromatic oil, an antioxidant, a compatibilizer, an adhesion promoter, a processing aid, and a combination thereof. In some embodiments, the filled composition is uncrosslinked. In some other embodiments, the filled composition is cross-linkable, and the additive package further comprises an initiator, a curing agent, an accelerator, or a combination thereof.

[0011] In the filled composition, the at least one polymer ingredient constitutes from about 0.4 weight percent (wt.%) to about 35 wt.%, the at least one metal-containing filler constitutes from about 50 wt.% to about 95.5 wt.%, and the additive package constitutes from about 0.1 wt.% to about 15 wt.%. In some embodiments, the at least one polymer ingredient is in the range of from about 1 wt.% to about 25 wt.%, for example, from about 10 wt.% to about 15 wt.%. The at least one metal-containing filler is in the range of from about 60 wt.% to about 95 wt.%, for example, from about 75 wt.% to about 85 wt.%. The additive package is in the range of from about 4 wt.% to about 15 wt.%, for example, from about 5 wt.% to about 10 wt.%. In some embodiments, the additive package comprises a paraffinic oil in the range of from about 5 wt.% to about 9 wt.% of the filled composition.

[0012] The present disclosure also provides a filled sheet for radiation shielding, comprising the filled composition as described. In some embodiments, for example, the filled sheet comprises from about 0.4 wt.% to about 35 wt.% of at least one polymer ingredient, from about 50 wt.% to 95.5 wt.% of at least one metal-containing filler, and from about 0.1 wt.% to about 15 wt.% of an additive package. The at least one polymer ingredient is selected from the group consisting of a polyolefin elastomer, a polyolefin co-polymer, a polyolefin ter-polymer, and a combination thereof. The polyolefin elastomer, the polyolefin co-polymer, or the polyolefin ter-polymer comprises monomer units derived from ethylene and at least one vinyl monomer having more than three carbon atoms, from example, from four to ten carbon atoms. Examples of the at least one polymer ingredient include but are not limited to a polyolefin elastomer (POE) and an olefin block copolymer (OBC) as described above.

[0013] The at least one metal-containing filler is selected from a metal filler, a metal compound and a combination thereof. For example, the at least one metal-containing filler comprises Sb, W, Ba, Pb, Bi, an alloy thereof, an oxide thereof, a salt thereof, or a combination thereof. The additive package comprising an additive selected from the group consisting of a paraffinic oil, an aromatic oil, an antioxidant, a compatibilizer, an adhesion promoter, a processing aid, and a combination thereof. The filled sheet can be uncrosslinked. In some other embodiments, the filled sheet can be crosslinkable or crosslinked. A crosslinkable filled sheet can further comprise an initiator, a curing agent, and/or accelerator.

[0014] The present disclosure also provides a protective garment for radiation shielding, comprising a filled composition described above. In some embodiments, the protective garment further comprises at least one layer of fabric such as nylon, polyester and combinations thereof. For example, in some embodiments, the protective garment comprises two outer layers of fabric, which encase one or more inner layers of a filled sheet. The protective garment can be in a suitable design including but are not limited to a vest-skirt apron, a frontal apron, and a dental apron. In some embodiments, the filled composition in the protective garment is uncrosslinked. In some other embodiments, the filled composition is crosslinked.

[0015] The filled composition and filled sheet have high efficiency in shielding or blocking radiation, excellent abrasion resistance, flexibility, and environmental stress cracking resistance, for example, after exposure to isopropyl alcohol. The protective garment is configured to shield radiation, for example, blocking X-rays, and is expected to survive the normal use for more than two years.

[0016] The present disclosure also provides method of making the filled composition, the filled sheet and the protective garment described above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The present disclosure is best understood from the following detailed description when read in conjunction with the accompanying drawings. It is emphasized that, according to common practice, the various features of the drawings are not necessarily to scale. On the contrary, the dimensions of the various features are arbitrarily expanded or reduced for clarity. Like reference numerals denote like features throughout specification and drawings.

FIGS. 1A-1C illustrate different styles of X-ray blocking aprons in accordance with some embodiments.
FIG. 2A is a diagram illustrating a layer construction of X-ray blocking garment in accordance with some embodiments.
FIG. 2B is a detailed illustration of a filled polymer sheet, showing likely surface structure.
FIGS. 3A-3B illustrate potential surface problems with the existing products.
FIGS. 4A-4B, 5A-5B and 6A-6B illustrate holes and cracks in existing X-ray protection garments.
FIG. 7 illustrates a method of making a filled sheet for blocking irradiation such as X-ray in accordance with some embodiments.
FIG. 8 shows the relationship between flex cycles to rupture and thickness of the filled sheets of some Comparative Examples and Examples.
FIG. 9 shows the relationship between rate of crack growth and thickness of the filled sheets of the Comparative Examples and some Examples.
FIG. 10 is a schematic illustration showing a "Tick Tock" flex tester incorporating abrasive surface.
FIG. 11 shows the superior abrasion resistance of the filled sheets provided in this disclosure.

DETAILED DESCRIPTION

[0018] This description of the exemplary embodiments is intended to be read in connection with the accompanying drawings, which are to be considered part of the entire written description. In the description, relative terms such as "lower," "upper," "horizontal," "vertical,", "above," "below," "up," "down," "top" and "bottom" as well as derivative thereof (e.g., "horizontally," "downwardly," "upwardly," etc.) should be construed to refer to the orientation as then described or as shown in the drawing under discussion. These relative terms are for convenience of description and do not require that the apparatus be constructed or operated in a particular orientation. Terms concerning attachments, coupling and the like, such as "connected" refer to a relationship wherein structures are secured or attached to one another either directly or indirectly through intervening structures, as well as both movable or rigid attachments or relationships, unless expressly described otherwise.

[0019] The present disclosure provides a filled composition for blocking radiation such as X-rays, a resulting sheet comprising such a filled composition, a resulting protective garment comprising such a filled composition, and the methods of making the same. The resulting protective garments can include radiation protection garments such as X-ray blocking garments.

[0020] X-ray blocking garments can include vest-skirt combinations, frontal aprons, dental drapes, thyroid collars, gonad shields, and combinations thereof. FIGS. 1A-1C illustrate vest-skirt aprons, frontal aprons and dental aprons, respectively, in accordance with some embodiments. As shown in FIG. 2A, a garment 200 for blocking radiation such as X-rays comprises two major components: 1) at least one layer of fabric such as outer layers 204 and 206 of non X-ray blocking fabric, such as nylon or polyester, which encase 2) at least one filled sheet or layer 202 comprising one or more inner layers 208 of highly filled polymer/heavy metal composite sheet, which absorbs the X-rays. The layers 204, 206 and 208 are stitched together. Each layer has a suitable thickness. For example, each of inner layers 208 in the at least one filled sheet 202 can be 15-25 mils (i.e. 381-635 microns) thick. Each of the outer layers 204 and 206 of fabric can have a thickness in the range of from 10 mils to 12 mils (i.e. from 254 microns to 305 microns). As shown in FIG. 2B, the filled sheets or layers 202 are highly filled with different metal particles. The size of the metal particles can be at micron level, for example, in the range of from 1 micron to 70 microns. The metal particles may protrude from surface creating roughness, or even fall out leaving craters, as shown in FIG. 2B.

[0021] Feeling comfort while wearing the garment for long periods is important, as its significant weight, between 7 and 15 pounds, exerts much force on the body. Elastic and Velcro fasteners are often attached to the fabric to secure the garment and comfort the wearers. Some efforts have been tried to address the effects of the extra weight, especially on the neck and back. In addition, design features such as placement of elastic and Velcro fasteners at the waist help "lift" the apron off the back. However, elastic and Velcro fasteners may subject the sheet to additional forces and deformation, which can result in premature development of holes and tears. The threads used to attach the Velcro also wear away at the layer of sheet next to it. The integrity of the filled sheet is of great concern to wearers, as holes and tears can cause the wearer to be exposed to unwanted X-ray radiation.

[0022] Besides the forces on it resulting from elastic and Velcro fasteners, the filled sheet undergoes strain during normal course of use. For example, folding the arms and bending over at the waist strain the back of a vest, with a recent paper reporting as much as 20% elongation in studies of garments on the upper body. This level of strain may accelerate premature failure because it simultaneously stretches the filled sheet while abrading it against other layers of filled sheet, and the fabric. This is an especially aggressive situation, as the filled sheet may have edges of metal particles protruding from it, which scrape away the other layers of sheet, as shown in FIG. 3A. Over time, the material is worn away and/or particles fall out, forming craters (as shown in FIG. 3A), which lead to holes. As illustrated in a side view of FIG. 3B, the filled sheet may also have sharp edges and an uneven surface.

[0023] Human motion also affects the integrity of the filled sheet within the garment because of the resulting flexing. For example, when a person wearing a full frontal apron sits down, the sections of filled sheet in the lap region are creased about 90 degrees. The angle may exceed 90 degrees if the wearer leans forward while sitting. Repeated sitting /leaning forward causes repeated flexing of the filled sheet in the same area of the lap region which eventually results in one or more holes forming due to flex-cracking. Furthermore, thicker sheets are likely to flex-crack faster than thinner ones.

[0024] Another motion that wears away the filled sheet within a protective garment is repeatedly leaning over a table or other hard surface. This action rubs the filled sheets against each other and against the layer of fabric.

[0025] Consequently, facilities worldwide that use open beam X-ray equipment employ inspection procedures for holes and tears in X-ray blocking aprons. For example, a rejection model for defects may be proposed. A large study of the integrity of eighty-five lead aprons in a hospital might be performed. Thus, the material failure of these garments is a large-scale, ongoing and serious issue.

[0026] Manufacturers may guarantee an apron against material defects for a period of two years, as the quality of the care also affects its lifetime. The protective garments such as aprons are suggested to be hung on special hangers to avoid creases, which accelerate the development of holes and tears.

[0027] The use of incompatible cleaning fluids, such as alcohol, and improper procedures, such as using a washing machine, may also shorten the lifetime of a protective garment. X-ray blocking aprons may become soiled during normal use, as many procedures expose them to blood and other fluids. Manufacturers usually specify the safest and most effective cleaning method for their aprons. Alcohols are commonly used. However, many X-ray blocking compositions deteriorate upon exposure to alcohol, causing premature failure.

[0028] FIGS. 4A-4B, 5A-5B and 6A-6B show tears, holes and cracks developed in protective garments due to abuse and/or normal wear.

[0029] The inventor in the present disclosure has determined the cause to the problem of premature failure of a protective garment such as an apron, especially in the filled sheets, and has determined the solutions to such a problem. Such a premature problem results from the situation where the filled sheet is subjected to simultaneous application of 1) high strain, or elongations and 2) abrasion against itself and fabric. The filled composition and the filled sheet described in this disclosure display excellent mechanical properties including abrasion resistance and flex-cracking resistance. The filled composition and the filled sheet provided in this disclosure also display superior resistance to environmental stress cracking, for example, after exposure to alcohols for a long time. This disclosure also provides advantages with respect to processing and productivity of a filled sheet on a sheet extrusion line.

1. Filled Composition

[0030] A filled composition for radiation shielding comprises at least one polymer ingredient and at least one metal-containing, the polymer ingredient being selected from a polyolefin elastomer, a polyolefin co-polymer, a polyolefin ter-polymer, and a combination thereof. The polyolefin elastomer, the polyolefin co-polymer, or the polyolefin ter-polymer comprises monomer units derived from ethylene and at least one vinyl monomer being butene or having more than five carbon atoms, for example, five to ten carbon atoms. The at least one metal-containing filler is selected from a metal filler, a metal compound and a combination thereof.

[0031] In some embodiments, the at least one polymer ingredient comprises a polyolefin elastomer (POE). For example, the POE comprises a copolymer of ethylene, and at least one vinyl monomer being butene or having at least five carbon atoms. Examples of the at least one vinyl monomer include butene, pentene, hexene, heptene, octene and a combination thereof. In some embodiments, the at least one polymer ingredient comprises a polyolefin elastomer (POE) comprising a copolymer of ethylene and octene. One example of a POE is available under a trade name ENGAGE from Dow Elastomers. ENGAGE polyolefin elastomers (POEs) are created using INSITE technology, a single-site catalyst and solution process technology. The technology integrates metallocene catalysts, the constrained-geometry, single-site homogeneous catalysts, with its polyethylene solution process. The related POEs include ethylene-butene coploymer and ethylene-octene copolymers. The POEs have a narrow or moderate molecular weight distribution (MWD), a melt index at 190 °C in the range from 0.5 gm/10 min to 30 gm/10 min, a density in the range of from 0.857 to 0.910, a glass transition temperature of from -61 °C to -35 °C, a shore A hardness in the range of from 56-96, and a flexural modulus in the range from 3 MPa to 110 MPa.

[0032] In some embodiments, the at least one polymer ingredient comprises an olefin block copolymer (OBC) having alternating blocks of rigid and elastomeric segments. The OBC can be a copolymer of ethylene and at least one vinyl monomer being butene or having at least five carbon atoms. Examples of the at least one vinyl monomer include butene, pentene, hexene, heptene, octene and a combination thereof. One example of the at least one polymer ingredient comprises an olefin block copolymer (OBC) of ethylene and octene.

[0033] One example of an olefin block copolymer (OBC) can be available under a trade name INFUSE™ from Dow Elastomers. INFUSE™ olefin block copolymers (OBCs) are polyolefins with alternating blocks of hard (highly rigid) and soft (highly elastomeric) segments. The block structure of OBCs offers an advantaged performance balance of flexibility and heat resistance compared to random polyolefin copolymers. This type of polymers also has good abrasion resistance.

[0034] In some embodiments, the polymer ingredient can be a copolymer or ter-polymer of ethylene and another vinyl monomer being butene or having more than five carbon atoms, for example, from five to ten carbon atoms. Examples of the vinyl monomer include butene, pentene, hexene, heptene, and octene. The vinyl monomer can have a longer chain structure, and the polymer ingredient has high molecular weight and high melt index for good flexibility and toughness. The copolymer or terpolymer can be in a random, block or comb configuration.

[0035] In some embodiments, nonpolar polymers are preferred. In some embodiments, the polymer ingredient can comprise another monomer such as vinyl acetate. In some embodiments, the polymer ingredient is a blend of two or three polymers. In some embodiments, the at least one polymer ingredient further comprises an ethylene-vinyl acetate copolymer, an ethylene-propylene-diene (EPDM) ter-polymer, or a combination thereof. For example, the at least one polymer ingredient is a blend of an ethylene-octene copolymer mixed with an ethylene-vinyl acetate copolymer, or a blend of an ethylene-octene copolymer mixed with EPDM. If added, the ethylene-vinyl acetate (EVA) copolymer or EPDM is less than 30 wt.% of the at least one polymer ingredient used in the filled composition in some embodiments. For example, the content of EVA used is about 20 wt. % of total amount of the polymer ingredients in some embodiments.

[0036] The at least one metal-containing filler comprises a metal having an atomic number greater than 50. For example, the at least one metal-containing filler comprises Sb, W, Ba, Pb, Bi, an alloy thereof, an oxide thereof, a salt thereof, or a combination thereof. The salt can be a sulfate, a chloride, or a carbonate of such a suitable metal, and combinations thereof. In some embodiments, the at least one metal-containing filler can be substantially free of Pb, and comprises a filler selected from Sb, W, Bi, a barium salt such as $BaSO_4$, and a combination thereof.

[0037] The at least one metal-containing filler can have different combination. The combinations include but are not limited to a mixture of Sb and Bi, a mixture of Sb and W, a mixture of Sb and $BaSO_4$, and a mixture of Bi and $BaSO_4$, a mixture of Sb, Bi and $BaSO_4$, and any other combination. In some embodiments, the at least one metal-containing filler comprises Sb, W, Pb and $BaSO_4$. The use of lighter X-ray absorbing metals such as antimony and bismuth (other than lead) reduces weight, and also provide lead-free products. In some embodiments, the particle size of the at least one metal-containing filler has a particle size in the range from 0.1 micron to 74 microns, for example, in the range from 1 micron to 44 microns.

[0038] In some embodiments, the particle size of all the metal-containing fillers are less than or equal to 74 microns. Particle size can be tested on a sieve shaker. For example, the weight percentages of a sample retained on a 150 mesh screen (opening size of 103 microns), a 200 mesh screen (opening size of 74 microns) and a 325 mesh screen (opening size of 43 microns) are determined. Average weight percentage of the particles in these size ranges (95% confidence) can be tested for each of the at least one metal-containing filler. The filled sheet can tolerate a small amount of particles in the range of from 75 microns to 103 microns, but a large amount of these particles are not used because they may serve as stress concentration points, and possibly lead to defects and cracks.

[0039] The filled composition can further comprise an additive package comprising at least one additive. Examples of an additive include but are not limited to an oil additive, an antioxidant, a compatibilizer, an adhesion promoter, a processing aid, any other suitable additive and a combination thereof.

[0040] Examples of such an oil additive include but are not limited to a paraffinic oil, or an aromatic oil such as naphthenic oil. In some embodiments, such an oil additive is a paraffinic oil, which can comprise saturated rings and long paraffinic side chains. Such an oil additive can be available under trade name SUNOCO SUNPAR from Sunoco. An example of naphthenic oil can be available under trade name NYTEX from NYNAS U.S.A. Inc., Houston, Texas.

[0041] Some other suitable additive may include a compatibilizer or an adhesion promoter. Examples of a suitable compatibilizer or adhesion promoter include but are not limited to a polyethylene grafted with maleic anhydride, available under the trademark of FUSABOND® from DuPont. Some other additives can include a fiber filler for reinforcement, and/or self-lubrication. Examples of a suitable fiber filler such as microfibers include but are not limited fibers of nylons, polyester and fluoropolymer such as polytetrafluoroethylene, for example, available under TEFLON® from DuPont.

[0042] In some embodiments, the filled composition is uncrosslinked. The uncrosslinked filled composition can be recycled easily after use. In some other embodiments, the filled composition is cross-linkable, and the additive package further comprises an additive such as an initiator, a curing agent, an accelerator, and a combination thereof.

[0043] Such a composition can be crosslinked under heating or through moisture ambient conditions. Examples of a suitable initiator or accelerator include but are not limited to peroxides. In some embodiments, the cross-linkable composition can comprise a co-agent such a monomer or oligomer having C=C bonds (e.g., triallyl isocyanurate) to increase cross-linking degree.

[0044] In the filled composition, the at least one polymer ingredient is in the range of from about 0.4 wt.% to about 35 wt.%, the at least one metal-containing filler is in the range of from about 50 wt.% to about 95.5 wt.%, and the additive package is in the range of from about 0.1 wt.% to about 15 wt.%. In some embodiments, the at least one polymer ingredient is in the range of from about 1 wt.% to about 25 wt.%, for example, from about 10 wt.% to about 15 wt.%. The at least one metal-containing filler is in the range of from about 60 wt.% to about 95 wt.%, for example, from about 75 wt.% to about 85 wt.%. The additive package is in the range of from about 4 wt.% to about 15 wt.%, for example, from about 5 wt.% to about 10 wt.%.

[0045] The additive package can mainly comprise an oil additive. The other additives such as antioxidants and processing aids can be in the range of from about 0.1 wt.% to about 1 wt.%, for example, from about 0.2 wt.% to about 0.5%. In some embodiments, the additive package comprises an oil additive such as paraffinic oil in the range of from about 5 wt.% to about 9 wt.% of the filled composition.

2. Processing and Filled Sheet

[0046] Some embodiments also provide a method of making the filled composition as described. In some embodiments, such a method comprises steps of mixing, compounding, and pelletizing.

[0047] The filled composition as described can be used to make a filled sheet comprising such a filled composition. In some embodiments, such a method comprises steps of extruding and forming a sheet.

[0048] FIG. 7 illustrates an exemplary method 700 of making a filled sheet for blocking irradiation such as X-ray in accordance with some embodiments.

[0049] At step 702, the ingredients including the at least one polymer ingredient, the at least one metal-containing filler, and the additive package are mixed in a mixer, for example, a batch mixer.

[0050] At step 704, the ingredients are compounded to form a filled compound. The compounding can be performed on compounding equipment such as an extruder. Mixing temperatures can range from 240 to 385 °F. Mixing time length can range from 15 to 40 minutes. Rotor speed can range from 25 to 35 rpm.

[0051] At step 706, pellets can be formed on an extruder having pelletizer.

[0052] At step 708, a filled sheet can be extruded. The pellets are fed into the hopper of a single screw extruder operating at 10 to 65 rpm and temperatures from 240 to 385 °F. A filled sheet of desired thickness can be formed through a slotted die having a gap of a suitable dimension, for example, in the range from 25 mils to 27 mils.

[0053] At step 710, the extruded filled sheet is formed. The extruded sheet can be placed onto a set of rollers, which serve to chill the filled sheet.

[0054] In some embodiments, such a method can also comprise a step of curing the composition if the filled composition is designed to be cross-linkable. For example, a heating step can be used to cure the polymer ingredient in a filled composition comprising peroxide.

[0055] At step 712, the filled sheet can be finished.

[0056] Formation of sheet from the filled compositions is not limited to the above-described method. Variations of this method include the use of a twin screw extruder to form the pellets, or to make sheet directly, and use of a calendaring process to form sheet from pellets.

[0057] The resulting filled sheet comprises a filled composition as described. For example, in some embodiments, the filled sheet comprises from about 0.4 wt.% to about 35 wt.% of at least one polymer ingredient, from about 50 wt.% to 95.5 wt.% of at least one metal-containing filler, and from about 0.1 wt.% to about 15 wt.% of an additive package.

[0058] The at least one polymer ingredient is selected from the group consisting of a polyolefin elastomer, a polyolefin co-polymer, a polyolefin ter-polymer, and a combination thereof. The polyolefin elastomer, the polyolefin co-polymer, or the polyolefin ter-polymer comprises monomer units is derived from ethylene and at least one vinyl monomer having more than three carbon atoms. In some embodiments, the at least one polymer ingredient comprises a polyolefin elastomer (POE). The POE can be a copolymer of ethylene and at least one vinyl monomer selected from the group consisting of butene, pentene, hexene, heptene, octene and a combination thereof. In some embodiments, the at least one polymer ingredient comprises an olefin block copolymer (OBC). The OBC can be a copolymer of ethylene and at least one vinyl monomer selected from the group consisting of butene, pentene, hexene, heptene, octene and a combination thereof.

[0059] The at least one metal-containing filler is selected from a metal filler, a metal compound or a combination thereof. For example, the at least one metal-containing filler comprises Sb, W, Ba, Pb, Bi, an alloy thereof, an oxide thereof, a salt thereof, or a combination thereof. The additive package comprising an additive selected from the group consisting of a paraffinic oil, an aromatic oil, an antioxidant, a compatibilizer, an adhesion promoter, a processing aid, and a combination thereof.

[0060] The filled sheet can be uncrosslinked. In some other embodiments, the filled sheet can be crosslinkable or crosslinked. A crosslinkable filled sheet can further comprise an initiator, a curing agent, and/or accelerator. The crosslinkable filled sheet becomes a crosslinked filled sheet after the polymer ingredients are cured (cross-linked).

3. Protective Garment

[0061] The filled sheet comprising a filled composition described above is used to make a protective garment for radiation shielding. In some embodiments, as described the filled composition in the protective garment comprises from about 0.4 wt.% to about 35 wt.% of at least one polymer ingredient, from about 50 wt.% to 95.5 wt.% of at least one metal-containing filler, from about 0.1 wt.% to about 15 wt.% of an additive package. The at least one polymer ingredient, selected from the group consisting of a polyolefin elastomer, a polyolefin co-polymer, a polyolefin ter-polymer, and a combination thereof. The polyolefin elastomer, the polyolefin co-polymer, or the polyolefin ter-polymer comprises monomer units derived from ethylene and at least one vinyl monomer having more than three carbon atoms. Examples of the at least one polymer ingredient include but are not limited to a polyolefin elastomer (POE) and an olefin block copolymer (OBC) as described.

[0062] In some embodiments, the protective garment further comprises at least one layer of fabric such as nylon, polyester and combinations thereof, as shown in FIG. 2A. For example, in some embodiments, the protective garment comprises two outer layers of fabric 204 and 206, which encase one or more inner layers 208 of filled sheet 202. The exemplary dimensions of different layers are described in FIG. 2A. In some embodiments, several layers of thin sheets 208 are used together, to achieve the desired level of radiation protection. Compared to using one thick filled sheet, the construction with several layers of thin sheets 208 can reduce flexing caused by human motion.

[0063] The protective garment can be in a suitable design including but are not limited to a vest-skirt apron, a frontal apron, and a dental apron as shown in FIGS 1A-1C. The filled composition in the protective garment can be uncrosslinked or crosslinked.

[0064] The protective garment can also comprise elastic and Velcro fasteners, which are attached to layers of fabric to secure the protective garment to a wearer's body.

[0065] Some embodiments also provide a method of making a protective garment comprising such a filled polymer composition as described, or a protective garment comprising a sheet comprising the filled polymer composition as described.

[0066] The filled composition and filled sheet have high efficiency in shielding or blocking radiation, excellent abrasion resistance, flexibility, and environmental stress cracking resistance, for example, after exposure to isopropyl alcohol. The protective garment is configured to shield (or block) radiation, for example, blocking X-rays. The resulting protective garments provide protections to related personnel in dental or medical examination, laboratory and industrial operation, and are expected to last more than two years during normal use.

4. Examples

[0067] The following ingredients were used in making the filled compositions (Examples Ex.1-12) shown in Table 1.

[0068] ENGAGE 8150 is a polyolefin elastomer (POE) from Dow Elastomers, which is manufactured using metallocene catalysts, the single-site catalysts, with its polyethylene solution process. ENGAGE 8150 is an ethylene-octene copolymer, having a density of 0.868 g/cm^3, and a melt index of 0.5 g/10 min at 190 °C (under 2.16 Kg).

[0069] INFUSE 9000 is an olefin block copolymer (OBC) of ethylene and octene, available from Dow Elastomers. INFUSE 9000 has a density of 0.877 g/cm^3, and a melt index of 0.5 g/10 min at 190 °C (under 2.16 Kg).

[0070] ELVAX 265 is an ethylene-vinyl acetate (EVA) copolymer resin having 28 wt.% of vinyl acetate comonomer content, available from DuPont. ELVAX 265 has a density of 0.951 g/cm^3, and a melt index of 3 g/10 min at 190 °C (under 2.16 Kg).

[0071] NORDEL IP 3745 is an EPDM terpolymer, available from Dow Elastomer. NORDEL IP 3745 comprises monomer units derived from ethylene (70 wt.%), propylene (30.5 wt.%) and ethylidene norbornene (ENB, 0.5 wt.%), and has a Mooney viscosity of 45 (ML 1+4 at 125°C).

[0072] Lead particles were obtained from Atomized Product Group, Garland, Texas. Its particle size with 95% confidence is less than 103 microns, with about 5 wt.% in the range of 75-103 microns, about 18 wt.% in the range of 44-74 microns, and about 77 wt.% less than 44 microns.

[0073] Barium sulfate particles were obtained from Cimbar Performance Minerals, Chatsworth, Georgia. Its particle size with 95% confidence is less than 44 microns.

[0074] Tungsten particles were obtained from Buffalo Tungsten Depew, New York. Its particle size with 95% confidence is less than 74 microns, with about 14 wt.% in the range of 44-74 microns, and about 86 wt.% less than 44 microns.

[0075] Bismuth particles were obtained from 5N Plus Wellingborough, UK or Acupowder, Union, New Jersey. Its particle size with 95% confidence is less than 74 microns, with about 26 wt.% in the range of 44-74 microns, and about 74 wt.% less than 44 microns.

[0076] Antimony particles were obtained from 5N Plus Wellingborough, UK or Acupowder, Union, New Jersey. Its particle size with 95% confidence is less than 74 microns, with about 16 wt.% in the range of 44-74 microns, and about 84 wt.% less than 44 microns.

[0077] SUNPAR 2280 oil is paraffinic oil comprising saturated rings and long paraffinic side chains, available from Sunoco.

[0078] NYTEX 5450 oil is naphthenic process oil comprising hydrotreated heavy naphthenic distillate, available from NYNAS U.S.A. Inc., Houston, Texas.

[0079] BNX 1225 is an antioxidant and thermal stabilizer blend comprising a primary and a secondary antioxidant, available from Mayzo, Inc, Suwanee, Georgia.

[0080] KEMAMIDE U is a processing aid or slip agent comprising oleamide, available from Chemtura Corporation, Middlebury, Connecticut.

[0081] The ingredients were first compounded to form pellets using a batch mixer and a pelletizing extruder. Mixing temperatures ranged from 116°C (240°F) to 196°C (385°F). Mixing times were 15 to 40 minutes. Rotor speed varied from 25 to 35 rpm. The pellets were subsequently fed into the hopper of a single screw extruder operating at 10 to 65 rpm and temperatures from 116°C (240°F) to 196°C (385°F). A filled sheet of desired thickness was formed through a slotted die having a gap of 25-27 mils, and then placed onto a set of rollers which served to chill it, after which it was analyzed for material properties.

[0082] The filled sheet of Example 10 (Ex.10) was formed by mixing the ingredients in a Haake 600 Mixer coupled with a Haake RC-90 Torque Rheometer followed by pressing to desired thickness using a Carver hydraulic press equipped with heated platens.

[0083] During extrusion of a highly filled composition, a "die clean" is generally performed after two rolls of sheets are produced. The reason is that a bead of liquid extrudate, commonly called "die drool," continuously and gradually builds up at the exit of the die. If not removed, the bead eventually breaks apart and forms whisker-like fragments on the sheet, resulting in defects. During a "die clean," the operator manually scrapes the drool off, a procedure which results in a loss of about 183 cm (6 feet) of sheet. However, during extrusion of the Examples, it was not necessary to clean the die after two rolls were produced. A die drool can be eliminated.

[0084] It was also observed using a digital X-ray machine that a filled sheet made from the Examples had a homogenous dispersion of the metal powder. This is also a processing advantage, as it reduces the amount of material that might be rejected due to nonuniformity, leading to increased "in-spec" output.

[0085] As shown in Table 2, six Comparative Examples of commercially available radiation blocking sheets are based on other polymers and additives. The lead equivalences of these sheets ranged from 0.125 to 0.25 mm based on the product specifications

[0086] The above-described X-ray blocking sheets were tested for one or more of the following: flex-crack resistance and rate of crack growth, abrasion resistance under variable levels of stress, tensile properties, tear strength, Durometer Shore A hardness, compressive modulus, drape coefficient, and resistance to isopropyl alcohol. The tensile properties include modulus of toughness and specific energy of absorption calculated from modulus of toughness and specific gravity.

(1) Flex Crack Resistance and Rate of Crack Growth

[0087] "Flex cracking" can be defined as a cracking condition of the surface of rubbery articles, resulting from repeated bending or flexing of the part. Flex crack resistance of a filled sheet without any pre-crack was evaluated on a DeMattia flex test apparatus developed by the Akron Rubber Development Laboratory (ARDL), following ASTM D 813. The method involved fatigue cycling at prescribed intervals followed by inspection of each specimen. A TeleSensory visual system consisting of a lens, image detection device, and screen, magnified the image at 36x. The length of a crack, which grew horizontal (parallel to the folding direction), was measured on the screen using a ruler.

[0088] Testing results of flex cycles to rupture were plotted against thickness of filled sheets of the comparative examples (commercial products) as shown in FIG. 8, and fitted to have an equation for prediction purpose. The result of flex cycles to rupture of a working example was compared to a corresponding predicted value based on the fitted equation and then a percentage increase was then calculated. Similarly, testing results of rates of crack growth were plotted against thickness of filled sheets of the comparative examples as shown in FIG. 9, and fitted to have an equation for prediction purpose. The result of rate of crack growth of a working example at a certain thickness was compared to a corresponding predicted value based on the corresponding fitted equation and then a percentage decrease was the calculated.

(2) Abrasion Resistance Under Variable Levels of Stress

[0089] "Abrasion resistance" is defined as the resistance of a material to loss of surface particles due to frictional forces. A testing procedure was developed to assess the resistance of a filled sheet to an especially aggressive situation: application of different amounts of stress during abrasion in combination with moderate flexing action.

[0090] A "Tick Tock" flex tester was employed and adapted for this purpose, as shown in FIG. 10. The test involved securing 14 x 150 mm strips of a filled sheet to the arm of the tester, attaching weights to the lower ends of the strips to achieve 1378 hPa (20 psi) to 6650 hPa (95 psi) and swinging (cycling) the arm back and forth through a 180 -degree arc with a 7.62 cm (3 inch) radius at a rate of 60 cycles per minute. The action rubbed both surfaces of the strip against two posts that were covered with P600 sandpaper with average grit size of 25.8 microns made by 3M. Eventually, most strips wore away and broke. A counter recorded the number of cycles to break a strip.

(3) Tensile Properties

[0091] Tensile properties of a filled sheet were tested following ASTM D412. Tensile properties obtained included the ultimate tensile strength, percent elongation at break, and elastic modulus. The area under the stress-strain curve was numerically integrated to determine the energy absorbed in deforming the rubbery sheet to its breaking point, which is also known as the "modulus of toughness." Measured values of the specific gravities of each material enabled the specific energy of absorption to be determined from the modulus of toughness.

(4) Tear Strength

[0092] Tear resistance was determined according to ASTM D-624, Die C (Graves). Die C produces a non-nicked sample. Rupture or tear initiation strength was measured at the stress concentration located at the 90° apex.

(5) Durometer Hardness, Shore A

[0093] Durometer hardness (Shore A) was measured following ASTM D 2240-05. The compressive moduli of the sheets were then estimated from the Durometer readings.

(6) Drape Coefficient

[0094] Drape is the ability of a fabric to fall under its own weight into wavy folds. The method of mass measurement for determination of the drape coefficient was employed to assess the tendency of several X-ray blocking sheets to form wavy ripples when worn. As an indicator of their relative stiffness, "drape coefficient" is defined as the fraction of the area of an annular ring placed concentrically above a draped fabric covered by the projection of the draped sample. The higher the drape coefficient a filled sheet has, the less drapeable or stiffer the filled sheet is. A material with a low drape coefficient is desirable.

[0095] In the experiment, a filled sheet was cut into circles of 32 cm (12.6 inches) in diameter and placed on a post of 9.7 cm (3.8 inches) in diameter and 18.4 cm (7.25 inches) in height. A light was mounted 195 cm (76.75 inches) above the filled sheet, and the shadows were traced onto paper for measurement. Drape coefficient was then calculated.

(7) Effect of Treatment with Isopropyl Alcohol: Comparison of Stress-Strain Plots and Drape Coefficient

[0096] The sensitivity of filled sheets to isopropyl alcohol was determined by measuring the changes in the tensile properties and drape coefficient. Filled sheets were soaked in 99% isopropyl alcohol for 10 and 60 minutes, respectively. After dried in air, the filled sheets were tested.

Table 1.

Composition	**Ex.1**	**Ex.2**	**Ex. 3**	**Ex. 4**	**Ex. 5**	**Ex. 6**	**Ex. 7**	**Ex. 8**	**Ex. 9**	**Ex. 10**	**Ex. 11**	**Ex. 12**
ENGAGE 8150	12.4	12	10.5	10.8	13.1	11.7	9.8		6.6	5.9		1
INFUSE 9000								13.9	6.6	5.9		
EL VAX 265							2.4				11.6	9.8
NORDEL IP 3745							0.1				0.5	0.4
Lead				28.7								29.1
Barium sulfate				4.3					71.2	43.9	0	4.3
Tungsten			24.5	1.3								1.4
Bismuth	16.9				16.9	17.2	16.9	16.6	10.8	13.2	16.7	
Antimony	62.1	79.9	57.8	47.1	62.1	62.9	62.7	64.6	0	25.8	64.9	47.7
SUNPAR 2280 oil	8.2	7.7	6.8	7.4	7.5	7.9	6.6	4.6	4.6	5		0.7
NYTEX 5450 oil							1.3				6.1	5.4
BNX 1225	0.2	0.2	0.2	0.2	0.2	0.2						
KEMAMIDE U	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.3	0.2	0.3	0.2	0.2
Total (wt.%)	100.0	100.0	100	100.0	100	100.0	100.0	100	100.0	100	100.0	100.0

Table 2.

Comparative Examples	Carrier
CEx1	PVC/plasticizer
CEx2	Rubber/oil
CEx3	PVC/plasticizer
CEx4	PVC/plasticizer
CEx5	PVC/plasticizer
CEx6	Rubber/oil

5. Testing Results:

[0097] Table 3 summarizes the testing results including tensile properties, tear resistance and hardness of the Examples (Ex. 1-11) and the Comparative Examples (CEx 1-6).

(1) Increased Flex Crack Resistance compared to Comparative Examples for the same sheet thickness

[0098] Table 4 shows results of flex-cracking from the mini-DeMattia flex test. The data of Comparative Examples were used for plotting and fitting the curve of FIG. 8.

[0099] Table 5 and Table 6 show the flex crack resistance and the crack growth rate of Examples 1-6. The data show that filled sheets formed from the compositions of Examples 1-6 require an average of 141% (ranging 18%-276%) more flex cycles to rupture, compared to filled sheet formed from the comparative controls (commercial products) at the same thickness. Filled sheets formed from the filled compositions provided in the present disclosure also grow flex cracks at a speed of an average of 72% (ranging from 55%-88%) slower compared to filled sheet formed from the comparative controls. Thus, the filled compositions in the present disclosure produce filled sheets with superior flex-crack resistance.

Table 3.

	CEx1	CEx2	CEx3	CEx4	CEx5	CEx6	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8	Ex.9	Ex.10	Ex.11
Ultimate Tensile Strength, psi	271	688	611	393	889	782	642	555	587	536	656	622	623	588	403	390	685
Percent Elongation at Break	164	408	224	232	47	331	897	793	909	912	842	855	775	798	644	660	604
5% Modulus, psi	107	199	221	37	208	133	102	97	92	182	-	-	-	-	-	-	211
Elastic Modulus, psi	1315	2405	2987	2106	3293	2044	1472	1940	1312	2400	-	-	-	-	-	-	2697
Modulus of Toughness psi	315	1519	987	614	288	1809	2833	2121	2669	2872	2898	2804	2664	2749	1593	1661	1955
Specific Energy of Absorption kJ/kg	0.6	2.8	1.5	1.2	0.6	3.3	7.2	5.5	6.0	6.4	7.1	7.0	6.4	6.4	4.4	4.1	4.3
Specific gravity	3.85	3.73	4.41	3.55	3.33	3.73	2.73	2.65	3.07	3.07	2.81	2.78	2.87	2.95	2.52	2.81	3.15
Tear Strength, lb/in	53	115	84	71	-	77	79	68	72	119	79	76	85	125	84	71	-
Shore A hardness	84	67	84	79	82	68	60	58	60	71	63	60	59	72	76	71	70
Compressive modulus, psi per (68)	2119	1137	2119	1769		1179	903	854	903	1316	991	903	877	1365	1584	1316	1268
Drape Coefficient % (thickness, mils)	21 (11.9)	32 (32.8)	31 (16.2)				25 (20)	25 (20)	24 (19)	19 (17)	27 (17.8)						

Table 4.

	CEx1	CEx2	CEx3	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6
Sheet Thickness, mil	11.9	21.1	26.2	20.0	20.0	23.8	18.9	19.8	19.6
Rate of crack growth inches/M cycles	0.13	0.32	0.79	0.041	0.13	0.10	0.13	0.043	0.12
Flex cycles to hole formation x10^5	6.2	2.8	1.2	11.0	6.5	4.4	4.1	12.0	5.7

Table 5.

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6
Sheet Thickness, mils	20	20	23.8	18.9	19.8	19.6
Flex cycles to hole formation x10^5	11	6.5	4.4	4.1	12	5.7
Predicted flex cycles to hole formation x10^5*	3.1	3.1	2.0	3.5	3.2	3.3
% Increase compared to prediction	252%	108%	115%	18%	276%	75%
* predictions from curve generated by current art data in FIG. 8						

Table 6.

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6
Sheet Thickness, mil	20	20	23.8	18.9	19.8	19.6
Rate of crack growth inches/M cycles	0.041	0.13	0.1	0.13	0.043	0.12
Predicted rate of crack growth inches/M cycles*	0.33	0.33	0.52	0.29	0.32	0.32
% Decrease compared to prediction	-88%	-61%	-81%	-55%	-87%	-62%
* predictions from curve generated by current art data in Figure 9						

(2) Increased Abrasion Resistance per mil at High Stress

[0100] Table 7 and FIG. 11 summarize the results of abrasion resistance. Table 8 shows results of average cycles to break per 0.0254 mm(mil) of sample thickness. (In the following data 1 psi equals 68.95 hPa).

[0101] At high levels of stress, some filled sheets formed from the filled compositions (Examples) in this disclosure failed to break, even after 120,000 to 130,000 cycles. Consequently, the experiments were ended at this point and the results were calculated. FIG. 11 also shows data points for Ex. 1 and Ex. 2 sheets abraded against a ripstock fabric (nylon/polyester), which is often used in garment construction. The results for abrasion against fabric and sandpaper are at the same order of magnitude; thus the P600 sandpaper is a realistic model surface for a fabric.

[0102] The filled sheets formed from the filled compositions (Examples) in this disclosure did not wear away and break as fast as the Comparative Examples when stress levels of 3447 hPa (50 psi) to 6650 hPa (95 psi) were applied during flex abrasion against P600 sandpaper. The filled sheet formed from the filled compositions of the Examples (e.g., Ex. 1-3, 7 and 11) required about 10 to 100 times the number of cycles per mil thickness to break in this stress range. Based on the stress-strain plots obtained, 3447 hPa (50 psi) to 6650 hPa (95 psi) imparts 5% of strain at most on the sheet. X-ray blocking garments likely experience such small levels of strain in everyday use.

[0103] As shown in Table 8, a blend of POE with approximately 20% EVA (Ex. 7) gave excellent abrasion resistance while a polymer ingredient consisting essentially of EVA copolymer (Ex. 11) displayed lower abrasion resistance compared to Ex. 7, but much better performance than the Comparative Examples.

Table 7.

CEx1		CEx2		Ex.1		Ex.2		Ex.3		Ex.7		Ex.11	
psi applied	cycles/mil to break	psi applied	cycles/mil to break	psi applied	cycles/mil to break	psi applied	cycles/mil to break	psi applied	cycles/mil to break	psi applied	cycles/mil to break	psi applied	cycles/mil to break
93	6	95	94	95	6147*	97	2861	96	3480	96	1451	95	241
73	18	75	46	75	6091*	75	5904*	74	5628*	75	3090	77	193
64	49	65	66	66	1390	65	5883*	66	2536*	64	453	67	86
52	62	50	81	50	110	51	1423	50	214	50	194	49	238
36	173	34	335	35	201	35	183	34	140	35	197	36	193
27	328	24	425	21	280	20	331	20	327	22	332	24	467

*One or more strips did not break after 120,000 to 130,000 flex cycles, whereupon the experiment was terminated

Table 8.

Stress Applied psi ± 2 psi	Average cycles/ mil thickness to break "Col. A" Plasticized PVC and Rubber/oil (CEx1, CEx2)	"Col. B" POE and POE/EVA (Ex. 1, Ex.2, Ex.3, Ex.7)	"Col C" EVA (Ex.11)	Comparison to Comparative Controls: Ratio of data in "Col. B"/ "Col. A"	Ratio of data in "Col. C" / "Col. A"
95	50	2597	241	52	5
75	32	3090	193	97	6
65	58	922	86	16	1
50	72	485	238	7	3

(3) Resistance to Alcohol

[0104] Table 9 shows tensile properties and drape coefficient of some Examples and Comparative Examples after immersion in isopropyl alcohol (99%, IPA) for 10 and 60 minutes, respectively. Table 10 shows the corresponding percent change of these properties following immersion in isopropyl alcohol (99%) for 60 minutes. As shown in Tables 9 and 10, the Examples (e.g., Ex. 1, Ex. 2) showed almost no change in tensile properties and drape coefficients after immersion in isopropyl alcohol for 60 minutes. The sheets of comparative examples (e.g., CEx1) formed from plasticized PVC showed substantial changes, for example, an increase of 172% in ultimate tensile strength, a decrease of 94% in elongation, an increase of 248% in drape coefficient and a decrease of 83% of specific energy of absorption. These changes indicate embrittlement, which was also observed by simply touching the treated sheet. The sheet formed from rubber/oil (e.g., CEx2) showed significant changes, particularly in ultimate tensile strength.

Table 9.

Time of immersion (mins) in isopropyl alcohol (IPA)	CEx1			CEx2			Ex.1			Ex.2		
	0	10	60	0	10	60	0	10	60	0	10	60
Ultimate Tensile Strength, psi	271	334	737	688	636	608	642	616	667	555	548	533
Percent Elongation at Break	164	17	10	408	395	392	897	889	868	793	788	783
Modulus of Toughness psi	315	63	43	1519	1432	1344	2833	2824	2922	2121	2108	2064
Specific Energy of Absorption kJ/kg	0.6	0.1	0.1	2.8	2.6	2.5	7.2	7.1	7.3	5.5	5.5	5.4
Drape Coefficient % (thickness, mils)	21 (12.2)	26	73	32 (32.8)	34	32	25 (20)	24	25	25 (20)	24	25

Table 10.

Percentage Change in Properties after immersion in IPA for 60 minutes	CEx1	CEx2	Ex.1	Ex.2
polymer/additive	plasticized PVC	rubber/oil	POE/oil	POE/oil
Ultimate Tensile Strength, psi	172	-12	4	-4
Percent Elongation at Break	-94	-4	-3	-1
Modulus of Toughness psi	-86	-12	3	-3
Specific Energy of Absorption kJ/kg	-83	-11	1	-2
Drape Coefficient %	248	-3		4

[0105] In summary, the filled composition and the filled sheet in the disclosure have excellent abrasion resistance, flexibility, and environmental stress cracking resistance. In addition, the filled composition and the filled sheet also have high efficiency in blocking radiation such as X-rays. The resulting protective garments can be used in related dental or medical examination, laboratory or industrial use, and are expected to last more than two years during normal use.

[0106] Although the subject matter has been described in terms of exemplary embodiments, it is not limited thereto. Rather, the disclosure should be construed broadly, to include other variants and embodiments, which may be made by those skilled in the art.

Claims

1. A filled composition for radiation shielding, comprising:

at least one polymer ingredient selected from the group consisting of a polyolefin elastomer, a polyolefin co-polymer, a polyolefin ter-polymer, and a combination thereof, wherein the polyolefin elastomer, the polyolefin co-polymer, or the polyolefin ter-polymer comprises monomer units derived from ethylene and at least one vinyl monomer being butene or having at least five carbon atoms; and
at least one metal-containing filler comprising a metal having an atomic number greater than 50.

2. The filled composition of claim 1, wherein
the at least one polymer ingredient comprises a polyolefin elastomer (POE).

3. The filled composition of claim 1, wherein
the at least one vinyl monomer has from five to ten carbon atoms.

4. The filled composition of claim 1, wherein
the at least one polymer ingredient comprises a polyolefin elastomer (POE), and the POE is a copolymer of ethylene and at least one vinyl monomer selected from the group consisting of butene, pentene, hexene, heptene, octene and a combination thereof.

5. The filled composition of claim 1, wherein
the at least one polymer ingredient comprises an olefin block copolymer (OBC) of ethylene and at least one vinyl monomer selected from the group consisting of butene, pentene, hexene, heptene, octene and a combination thereof.

6. The filled composition of claim 1, wherein
the at least one polymer ingredient comprises an olefin block copolymer (OBC) of ethylene and octene.

7. The filled composition of claim 1, wherein
the at least one vinyl monomer is selected from the group consisting of butene, pentene, hexene, heptene, and octene.

8. The filled composition of claim 1, wherein
the at least one metal-containing filler comprises Sb, W, Ba, Pb, Bi, an alloy thereof, an oxide thereof, a salt thereof, or a combination thereof.

9. The filled composition of claim 1, wherein the at least one metal-containing filler is substantially free of Pb, and comprises a filler selected from Sb, W, Bi, $BaSO_4$, or a combination thereof.

10. The filled composition of claim 1, further comprising: an additive package comprising an additive selected from the group consisting of a paraffinic oil, an aromatic oil, an antioxidant, a compatibilizer, an adhesion promoter, a processing aid, and a combination thereof.

11. The filled composition of claim 10, wherein the filled composition is cross-linkable, and the additive package further comprises an additive selected from the group consisting of an initiator, a curing agent, an accelerator, and a combination thereof.

12. The filled composition of claim 10, wherein
the at least one polymer ingredient constitutes from about 0.4 weight percent (wt.%) to about 35 wt.% of the filled composition;
the at least one metal-containing filler constitutes from about 50 wt.% to about 95.5 wt.% of the filled composition; and
the additive package constitutes from about 0.1 wt.% to about 15 wt.% of the filled composition.

13. The filled composition of claim 10, wherein the additive package comprises a paraffinic oil in the range of from about 5 wt.% to about 9 wt.%.

14. A filled sheet for radiation shielding, comprising the filled composition according to any one of the preceding claims.

15. A protective garment for radiation shielding, comprising the filled composition according to any one of claims 1-13.

Patentansprüche

1. Gefüllte Zusammensetzung zur Abschirmung gegen Strahlung, umfassend:

mindestens einen Polymerinhaltsstoff, ausgewählt aus der Gruppe bestehend aus einem Polyolefinelastomer, einem Polyolefincopolymer, einem Polyolefinterpolymer und einer Kombination davon,
wobei das Polyolefinelastomer, das Polyolefincopolymer oder das Polyolefinterpolymer von Ethylen abgeleitete Monomereinheiten und mindestens ein Vinylmonomer umfasst, das Buten ist oder mindestens fünf Kohlenstoffatome aufweist; und
mindestens einen metallhaltigen Füllstoff, der ein Metall mit einer Ordnungszahl größer als 50 umfasst.

2. Gefüllte Zusammensetzung nach Anspruch 1, wobei der mindestens eine Polymerinhaltsstoff ein Polyolefinelastomer (POE) umfasst.

3. Gefüllte Zusammensetzung nach Anspruch 1, wobei das mindestens eine Vinylmonomer fünf bis zehn Kohlenstoffatome umfasst.

4. Gefüllte Zusammensetzung nach Anspruch 1, wobei der mindestens eine Polymerinhaltsstoff ein Polyolefinelastomer (POE) umfasst, und das POE ein Copolymer von Ethylen und mindestens einem Vinylmonomer ist, ausgewählt aus der Gruppe bestehend aus Buten, Penten, Hexen, Hepten, Okten und einer Kombination davon.

5. Gefüllte Zusammensetzung nach Anspruch 1, wobei der mindestens eine Polymerinhaltsstoff ein Olefinblockcopolymer (OBC) von Ethylen und mindestens einem Vinylmonomer umfasst, ausgewählt aus der Gruppe bestehend aus Buten, Penten, Hexen, Hepten, Octen und einer Kombination davon.

6. Gefüllte Zusammensetzung nach Anspruch 1, wobei der mindestens eine Polymerinhaltsstoff ein Olefinblockcopolymer (OBC) von Ethylen und Octen umfasst.

7. Gefüllte Zusammensetzung nach Anspruch 1, wobei das mindestens eine Vinylmonomer aus der Gruppe bestehend aus Buten, Penten, Hexen, Hepten, und Octen ausgewählt ist.

8. Gefüllte Zusammensetzung nach Anspruch 1, wobei der mindestens eine metallhaltige Füllstoff Sb, W, Ba, Pb, Bi, eine Legierung davon, ein Oxid davon, ein Salz davon oder eine Kombination davon umfasst.

9. Gefüllte Zusammensetzung nach Anspruch 1, wobei der mindestens eine metallhaltige Füllstoff im Wesentlichen frei von Pb ist und einen Füllstoff ausgewählt aus Sb, W, Bi, $BaSO_4$ oder einer Kombination davon umfasst.

10. Gefüllte Zusammensetzung nach Anspruch 1, ferner umfassend: ein Zusatzpaket, umfassend einen Zusatzstoff, ausgewählt aus der Gruppe bestehend aus einem paraffinischen Öl, einem aromatischen Öl, einem Antioxidans, einem Kompatibilisator, einem Haftvermittler, einem Verarbeitungshilfsstoff und einer Kombination davon.

11. Gefüllte Zusammensetzung nach Anspruch 10, wobei die gefüllte Zusammensetzung vernetzbar ist, und das Zusatzpaket ferner einen Zusatzstoff umfasst, ausgewählt aus der Gruppe bestehend aus einem Initiator, einem Härter, einem Beschleuniger und einer Kombination davon.

12. Gefüllte Zusammensetzung nach Anspruch 10, wobei
der mindestens eine Polymerinhaltsstoff von etwa 0,4 Gewichtsprozent (Gew.-%) bis etwa 35 Gew.-% der gefüllten Zusammensetzung darstellt;
der mindestens eine metallhaltige Füllstoff von etwa 50 Gew.-% bis etwa 95,5 Gew.-% der gefüllten Zusammensetzung darstellt; und
das Zusatzpaket von etwa 0,1 Gew.-% bis etwa 15 Gew.-% der gefüllten Zusammensetzung darstellt.

13. Gefüllte Zusammensetzung nach Anspruch 10, wobei das Zusatzpaket ein paraffinisches Öl im Bereich von etwa 5 Gew.-% bis etwa 9 Gew.-% umfasst.

14. Gefüllte Flachstruktur zur Abschirmung gegen Strahlung, umfassend die gefüllte Zusammensetzung nach einem der vorhergehenden Ansprüche.

15. Schutzkleidung zur Abschirmung gegen Strahlung, umfassend die gefüllte Zusammensetzung nach einem der Ansprüche 1 bis 13.

Revendications

1. Composition chargée de radioprotection, comprenant :

au moins un ingrédient polymère choisi dans le groupe constitué d'un élastomère de polyoléfine, d'un copolymère de polyoléfine, d'un terpolymère de polyoléfine et d'une combinaison de ceux-ci, l'élastomère de polyoléfine, le copolymère de polyoléfine ou le terpolymère de polyoléfine comprenant des unités monomères dérivées d'ethylene et au moins un monomère vinylique étant le butène ou ayant au moins cinq atomes de carbone ; et
au moins une charge à base de métal comprenant un métal ayant un numéro atomique supérieur à 50.

2. Composition chargée selon la revendication 1, dans laquelle l'au moins un ingrédient polymère comprend un élastomère de polyoléfine (POE).

3. Composition chargée selon la revendication 1, dans laquelle l'au moins un monomère vinylique a de cinq à dix atomes de carbone.

4. Composition chargée selon la revendication 1, dans laquelle l'au moins un ingrédient polymère comprend un élastomère de polyoléfine (POE), le POE étant un copolymère d'ethylene et d'au moins un monomère vinylique choisi dans le groupe constitué de butène, de pentène, d'hexène, d'heptène, d'octène et d'une combinaison de ceux-ci.

5. Composition chargée selon la revendication 1, dans laquelle l'au moins un ingrédient polymère comprend un copolymère bloc oléfinique (OBC) d'ethylene et d'au moins un monomère vinylique choisi dans le groupe constitué de butène, de pentène, d'hexène, d'heptène, d'octène et d'une combinaison de ceux-ci.

6. Composition chargée selon la revendication 1, dans laquelle
l'au moins un ingrédient polymère comprend un copolymère bloc oléfinique (OBC) d'ethylene et d'octène.

7. Composition chargée selon la revendication 1, dans laquelle
l'au moins un monomère vinylique est choisi dans le groupe constitué de butène, de pentène, d'hexène, d'heptène et d'octène.

8. Composition chargée selon la revendication 1, dans laquelle
l'au moins une charge à base de métal comprend du Sb, du W, du Ba, du Pb, du Bi, un alliage de ceux-ci, un oxyde de ceux-ci, un sel de ceux-ci, ou une combinaison de ceux-ci.

9. Composition chargée selon la revendication 1, dans laquelle
l'au moins une charge à base de métal est sensiblement exempte de Pb et comprend une charge choisie parmi le Sb, le W, le Bi, le $BaSO_4$, ou une combinaison de ceux-ci.

10. Composition chargée selon la revendication 1, comprenant en outre :
une préformulation d'additifs comprenant un additif choisi dans le groupe constitué d'une huile paraffinique, d'une huile aromatique, d'un antioxydant, d'un agent de comptabilité, d'un promoteur d'adhésion, d'un adjuvant de fabrication et d'une combinaison de ceux-ci.

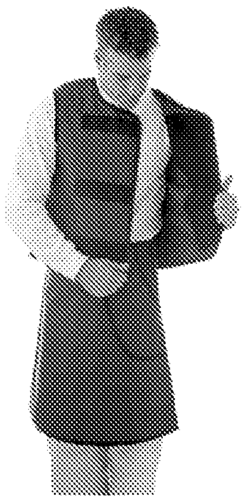
11. Composition chargée selon la revendication 10, dans laquelle
la composition chargée est réticulable, et la préformulation d'additifs comprend en outre un additif choisi dans le groupe constitué d'un initiateur, d'un agent de durcissement, d'un accélérateur et d'une combinaison de ceux-ci.

12. Composition chargée selon la revendication 10, dans laquelle
l'au moins un ingrédient polymère constitue d'environ 0,4 pour cent en poids (% en poids) à environ 35 % en poids de la composition chargée ;
l'au moins une charge à base de métal constitue d'environ 50 % en poids à environ 95,5 % en poids de la composition chargée ; et
la préformulation d'additifs constitue d'environ 0,1 % en poids à environ 15 % en poids de la composition chargée.

13. Composition chargée selon la revendication 10, dans laquelle
la préformulation d'additifs comprend une huile paraffinique dans la plage comprise entre environ 5 % en poids et environ 9 % en poids.

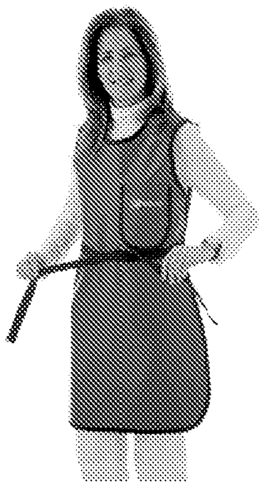
14. Feuille chargée de radioprotection, comprenant la composition chargée selon l'une quelconque des revendications précédentes.

15. Vêtement de radioprotection, comprenant la composition chargée selon l'une quelconque des revendications 1 à 13.



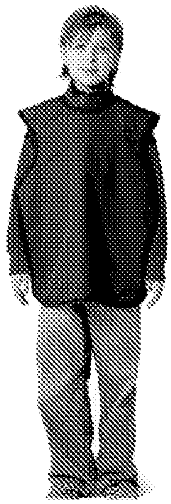
Vest-Skirt Apron

FIG. 1A



Frontal Apron

FIG. 1B



Dental Apron

FIG. 1C

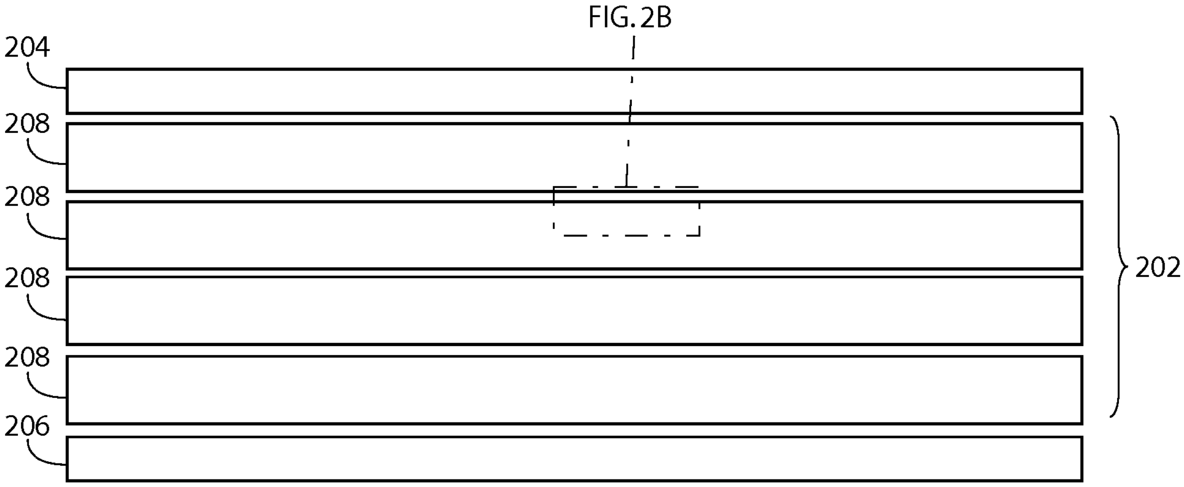


FIG. 2A

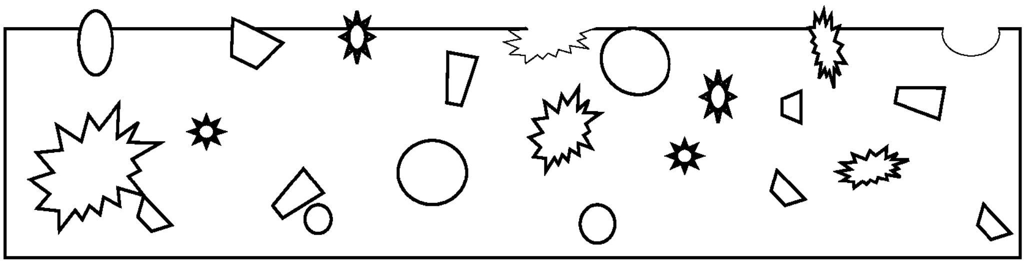


FIG. 2B

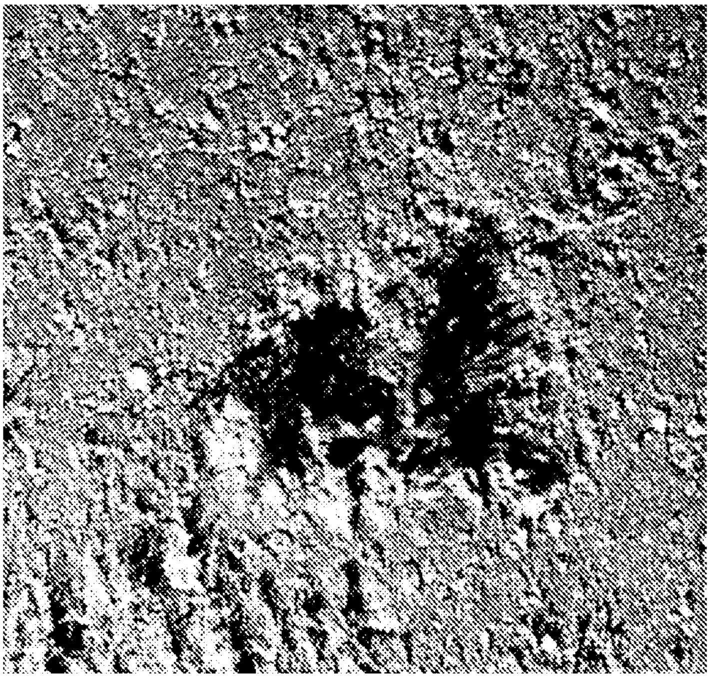


FIG. 3A

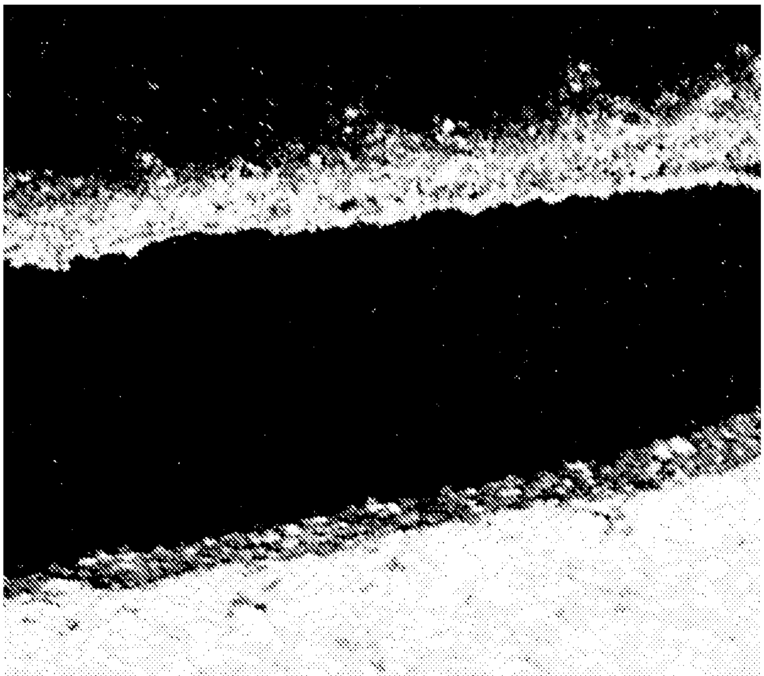


FIG. 3B

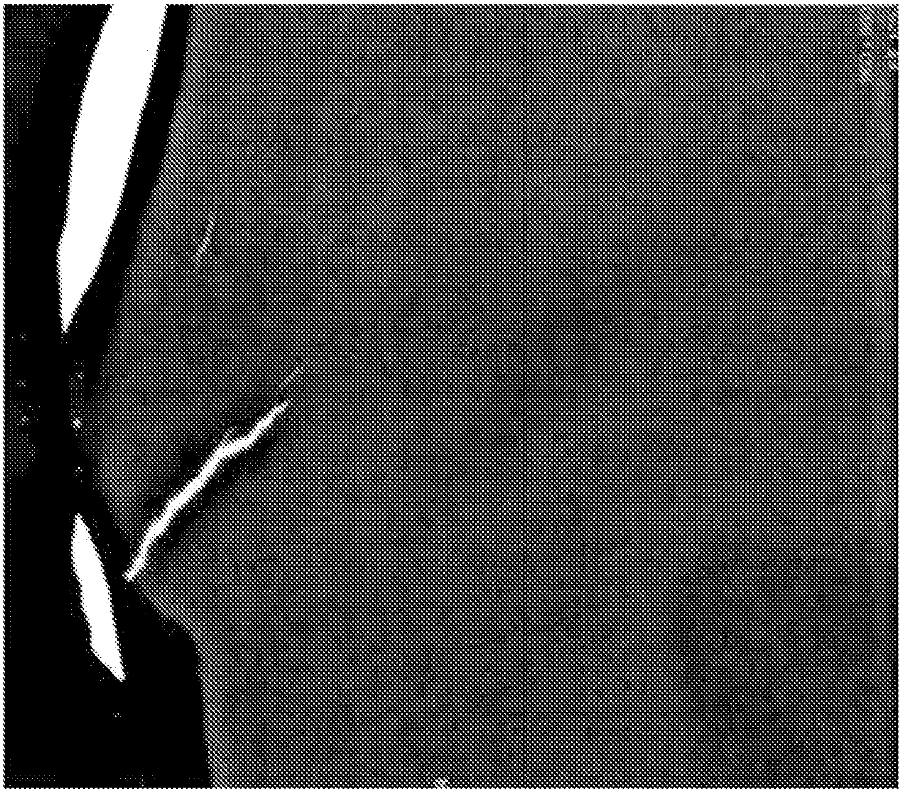


FIG. 4A

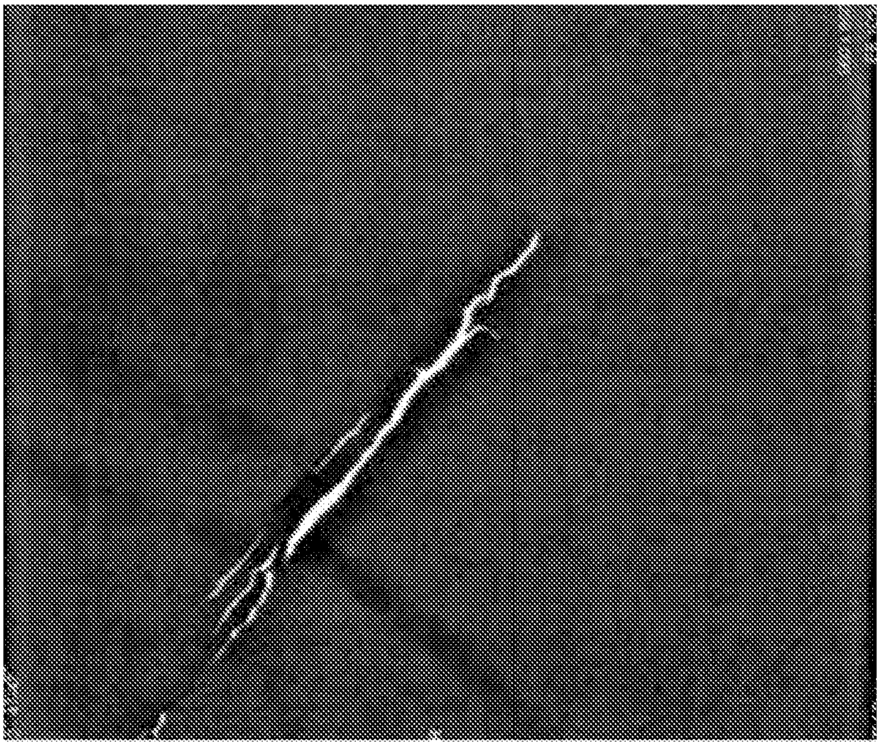


FIG. 4B

FIG. 5B

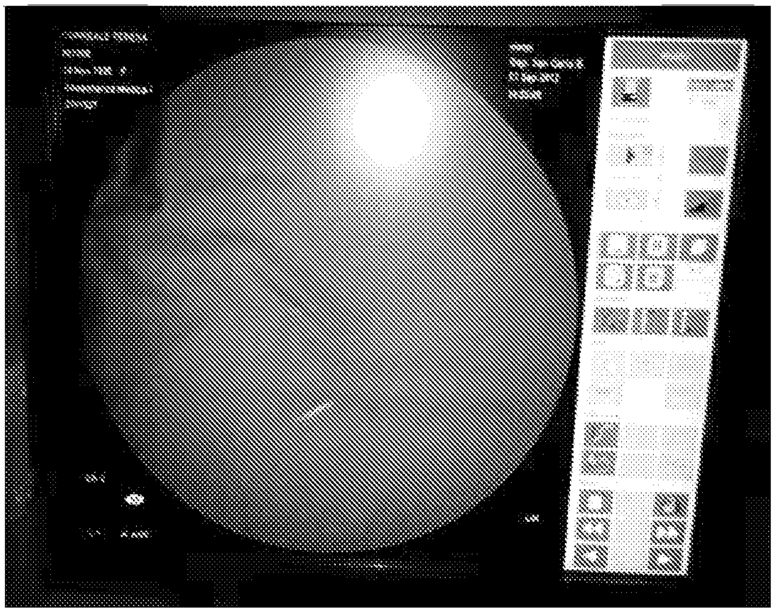


FIG. 5A

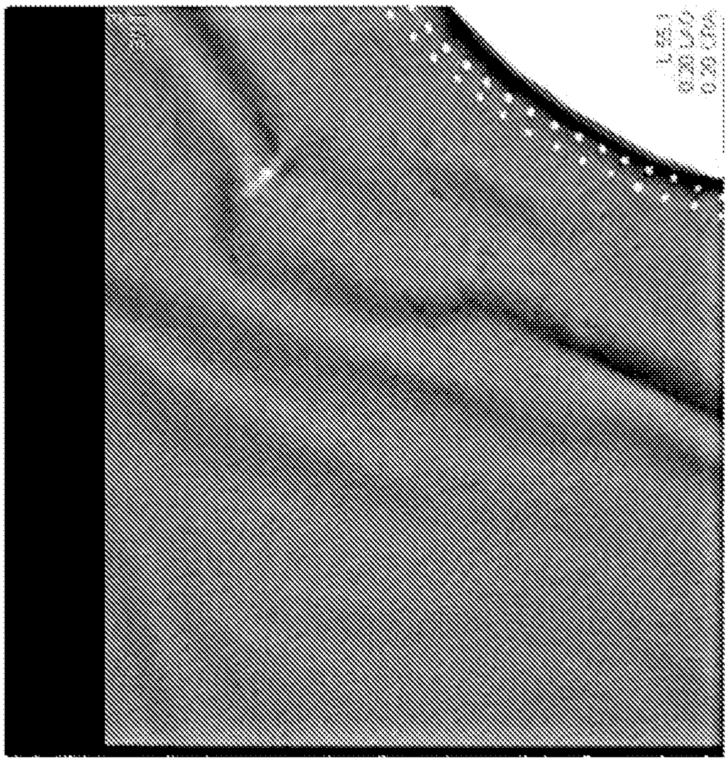


FIG.6B

FIG.6A

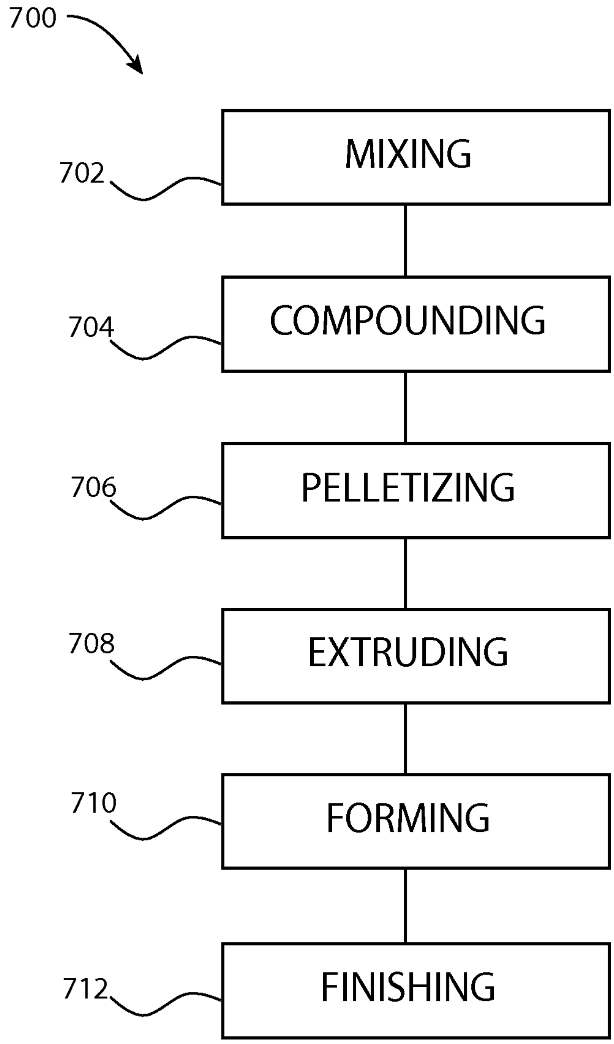

700
702
MIXING
704
COMPOUNDING
706
PELLETIZING
708
EXTRUDING
710
FORMING
712
FINISHING

FIG. 7

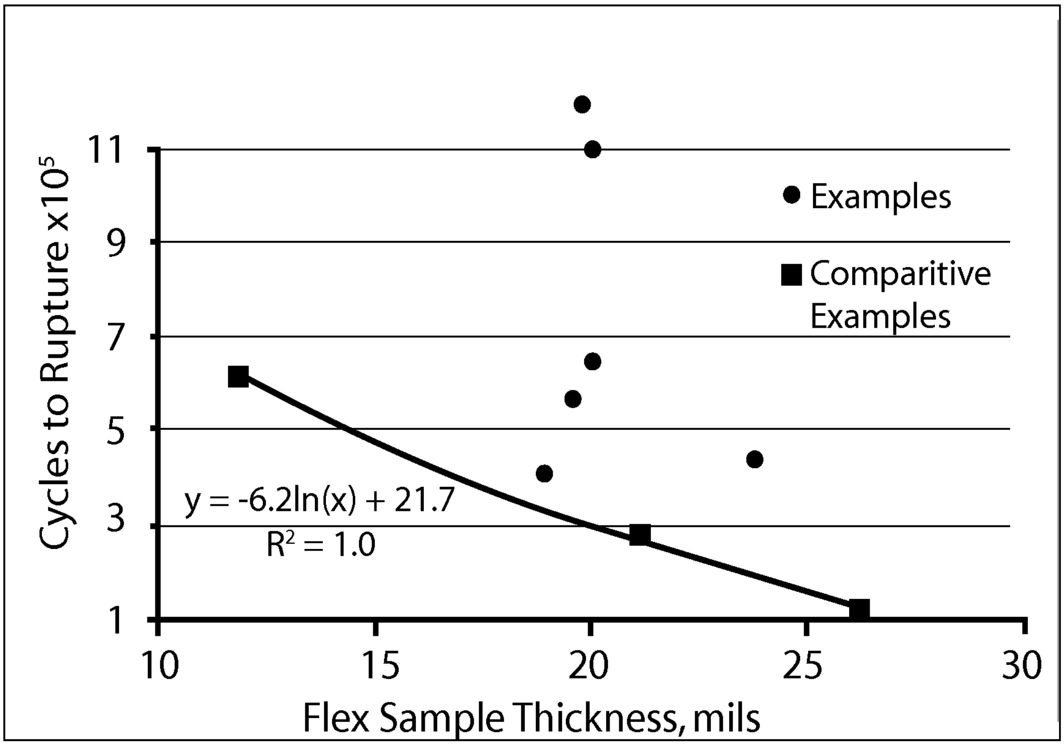
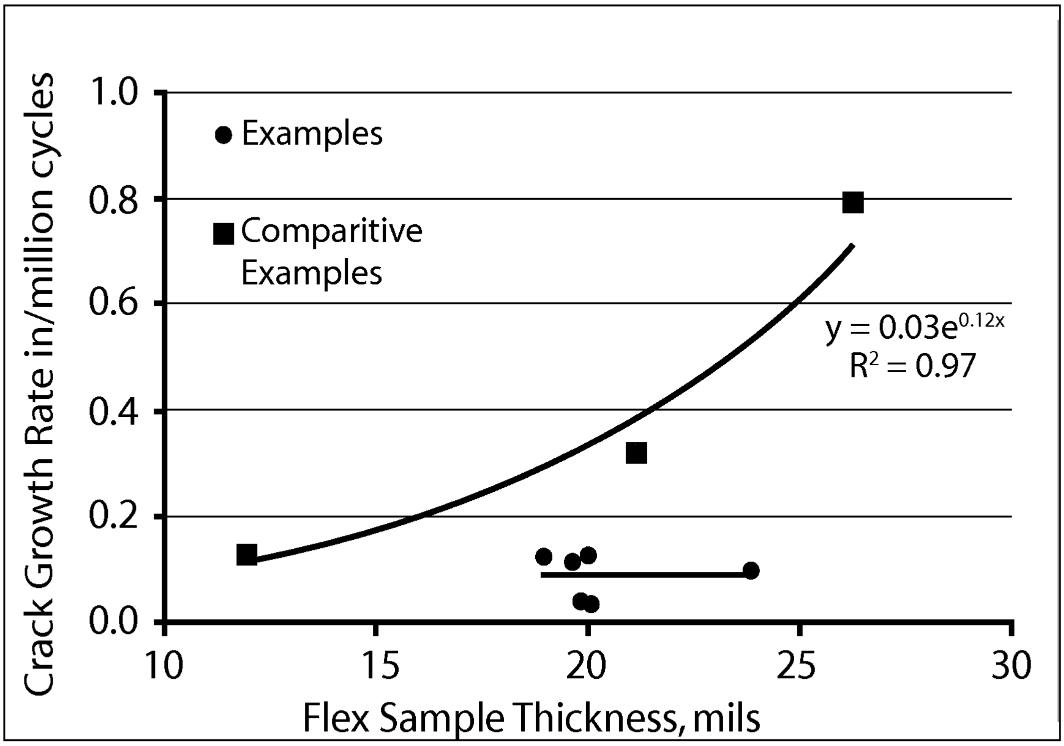

Cycles to Rupture x10^5
11
9
7
5
3
1
10
15
20
25
30
Flex Sample Thickness, mils
Examples
Comparitive Examples
y = -6.2ln(x) + 21.7
R² = 1.0

FIG. 8



1.0
0.8
0.6
0.4
0.2
0.0
Crack Growth Rate in/million cycles
● Examples
■ Comparitive Examples
y = 0.03e^0.12x
R² = 0.97
10
15
20
25
30
Flex Sample Thickness, mils

FIG. 9

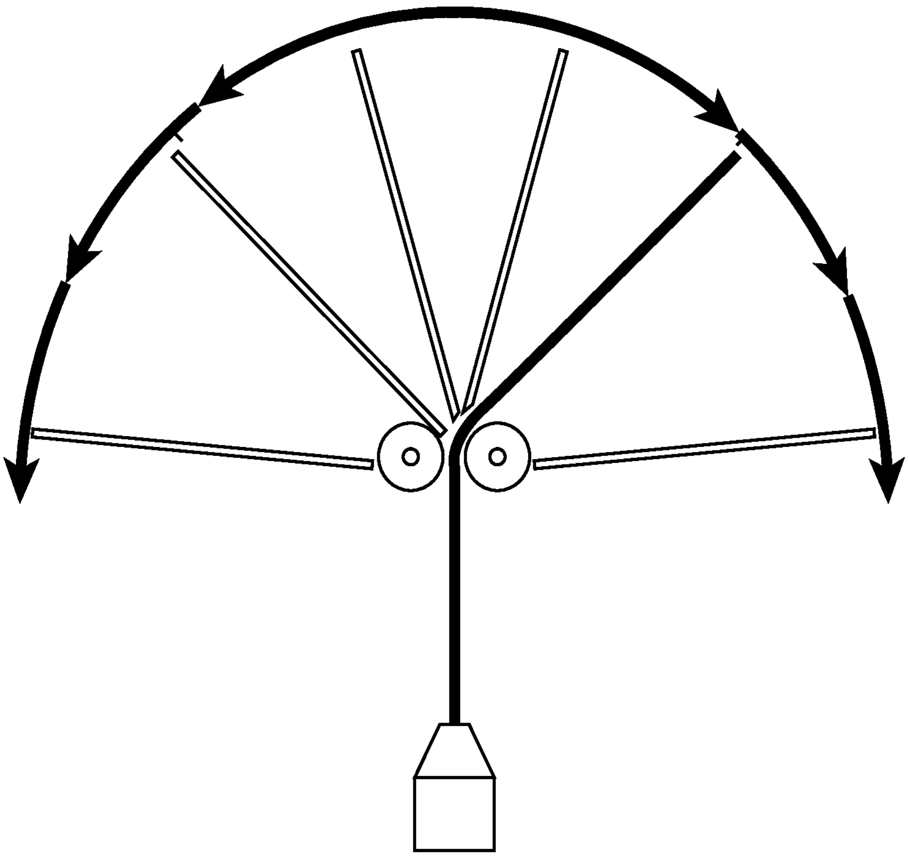
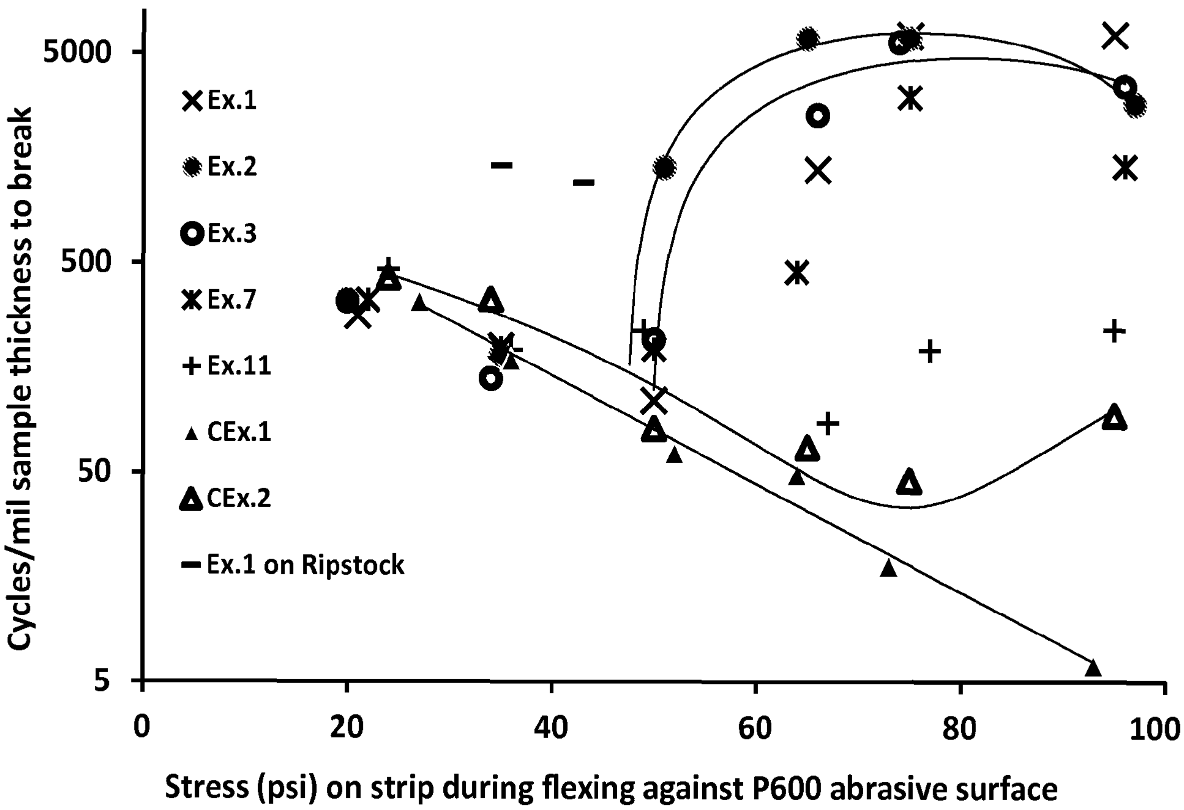


FIG. 10



5000
500
50
5
Cycles/mil sample thickness to break
Ex.1
Ex.2
Ex.3
Ex.7
Ex.11
CEx.1
CEx.2
Ex.1 on Ripstock
0
20
40
60
80
100
Stress (psi) on strip during flexing against P600 abrasive surface

FIG. 11

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 06829713 A **[0001]**
- US 61720553 A **[0001]**