

US 20130095307A1

(19) **United States**

(12) **Patent Application Publication**
BENNINGTON et al.

(10) **Pub. No.: US 2013/0095307 A1**

(43) **Pub. Date: Apr. 18, 2013**

(54) **SPACECRAFT AND SPACESUIT SHIELD**

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(21) Appl. No.: **13/274,871**

(22) Filed: **Oct. 17, 2011**

B32B 27/06 (2006.01)
B29C 47/06 (2006.01)
B29D 7/00 (2006.01)
B29C 70/28 (2006.01)
B28B 5/00 (2006.01)
G21F 1/10 (2006.01)
B32B 27/34 (2006.01)

(52) **U.S. Cl.**
USPC **428/213**; 252/478; 428/221; 428/515;
428/474.4; 428/473.5; 428/421; 264/212;
156/313; 264/639; 264/465

Publication Classification

(51) **Int. Cl.**
B32B 7/02 (2006.01)
B32B 3/00 (2006.01)

(57) **ABSTRACT**

A spacecraft or spacesuit that provides shielding to reduce exposure to ionizing radiation such as high energy electrons and protons. Further, methods are provided for reducing exposure through spacesuits and manufacturing spacecraft and spacesuit shields.





Figure 1a

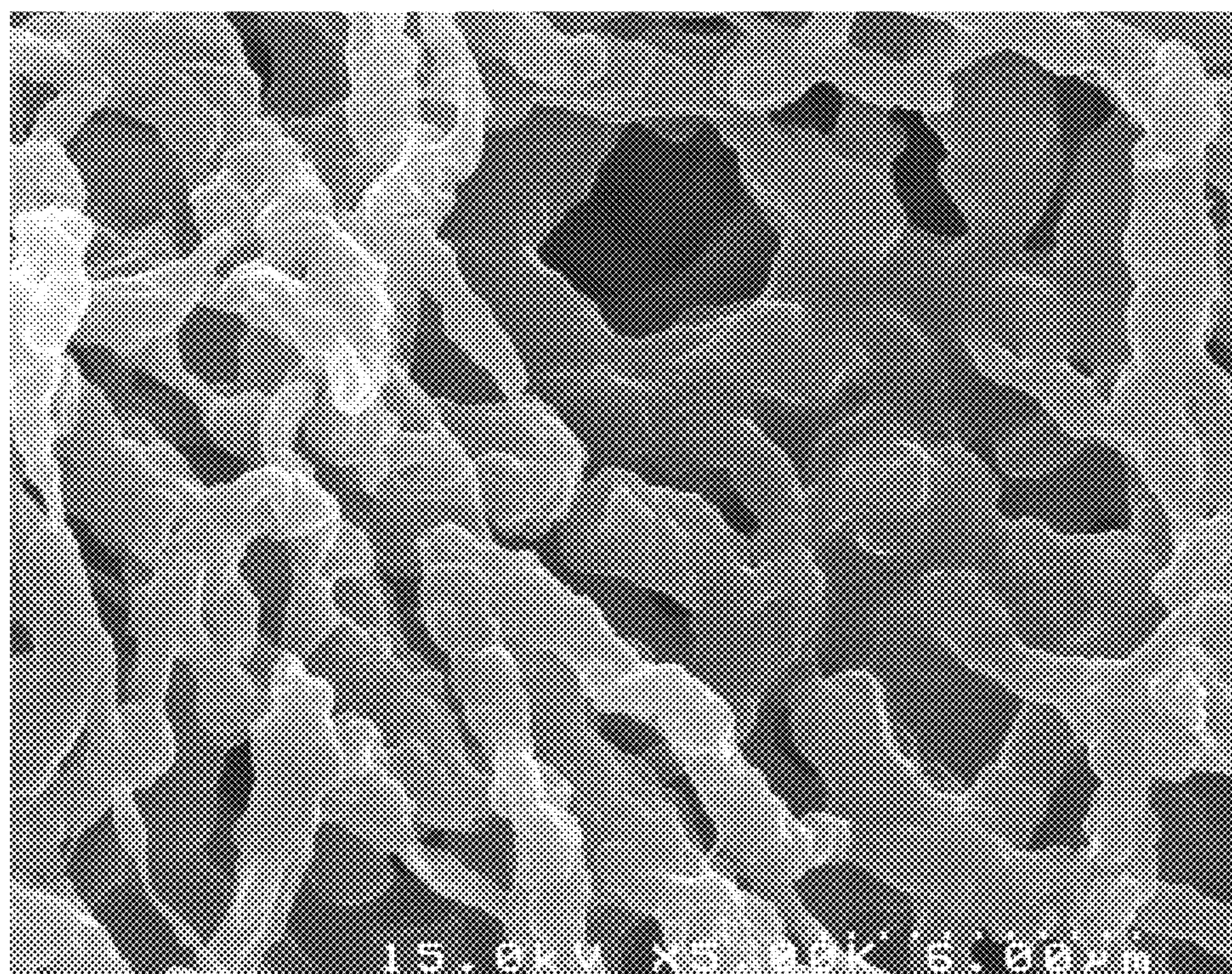


Figure 1b



Figure 1c

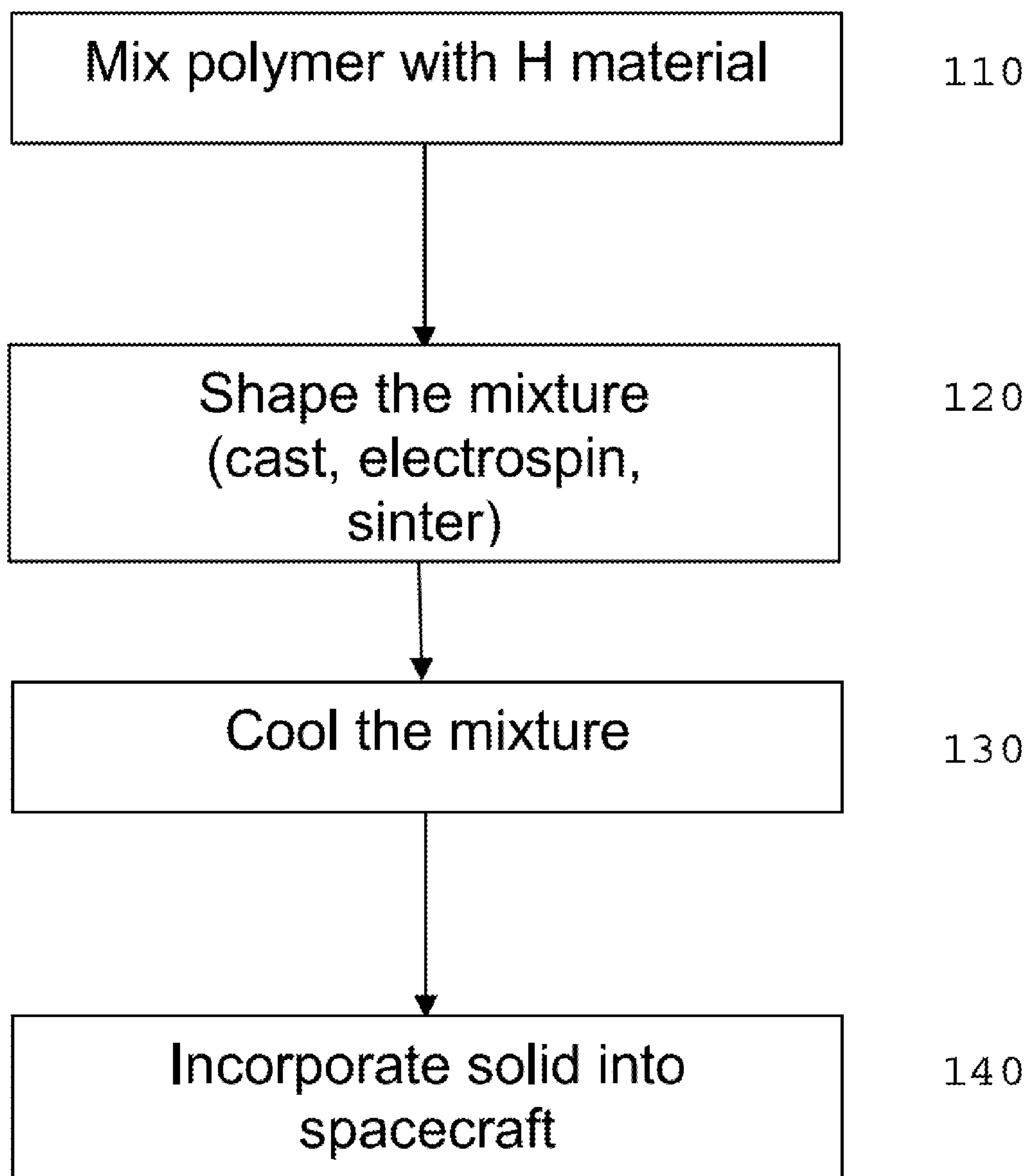


Figure 2

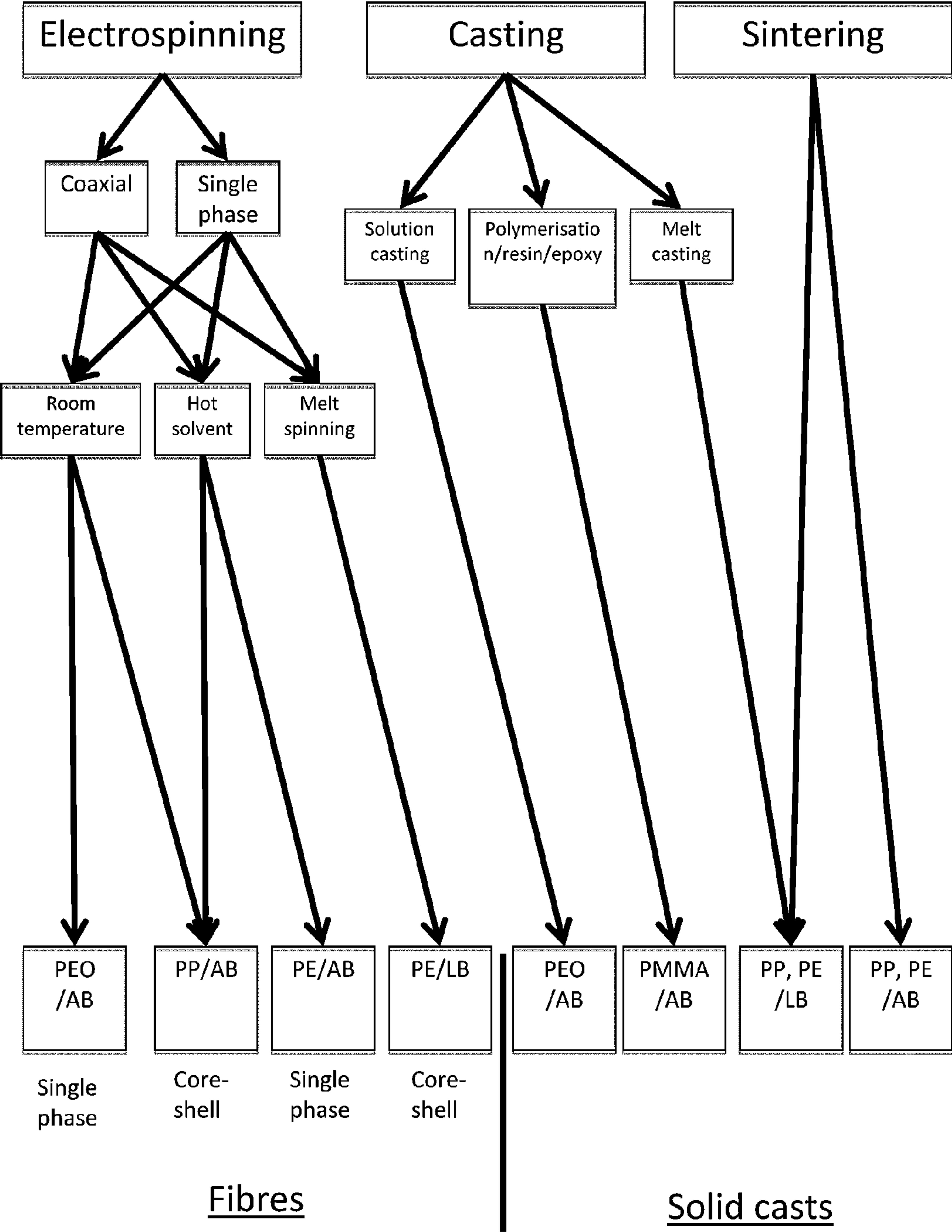


Figure 3

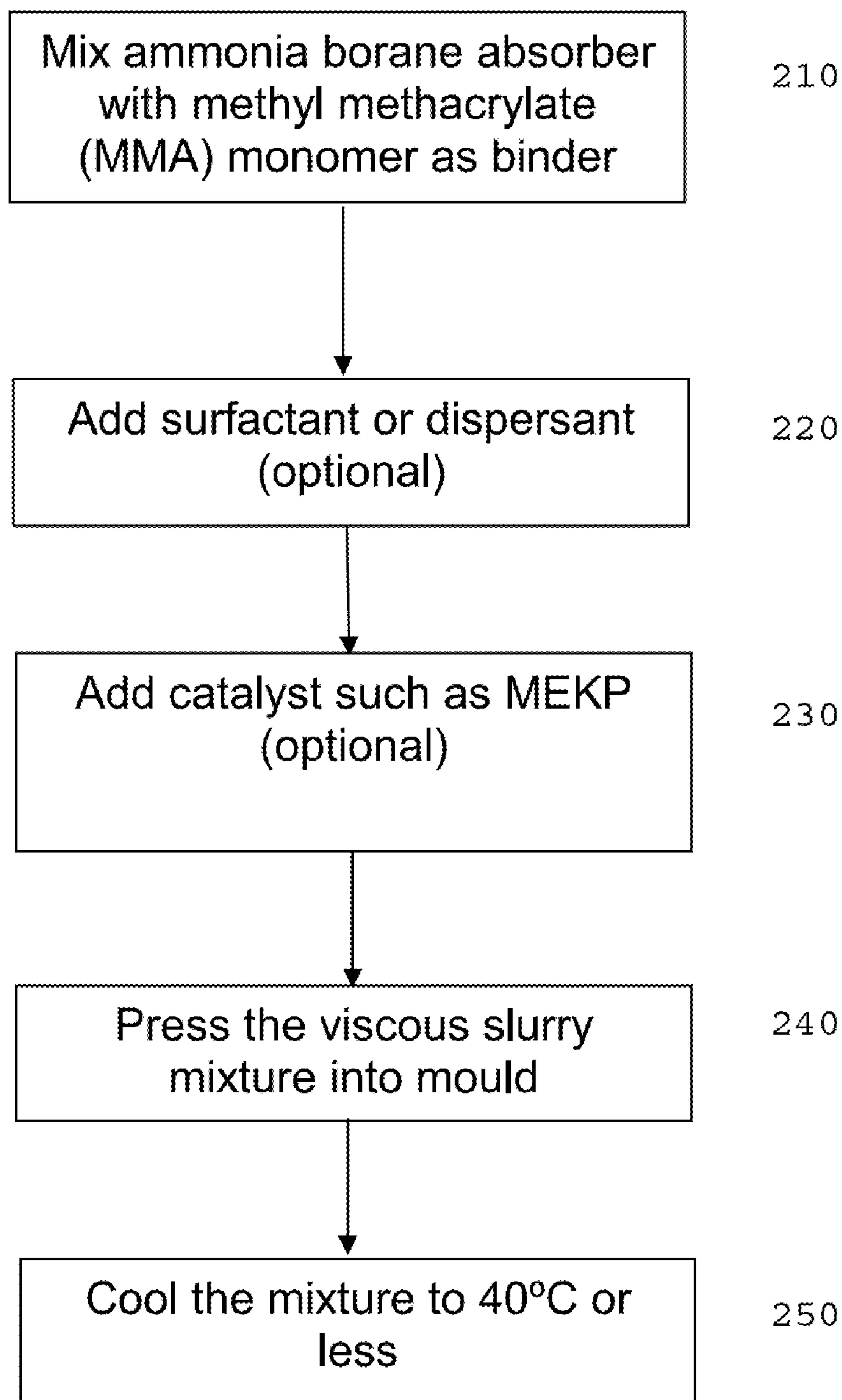


Figure 4

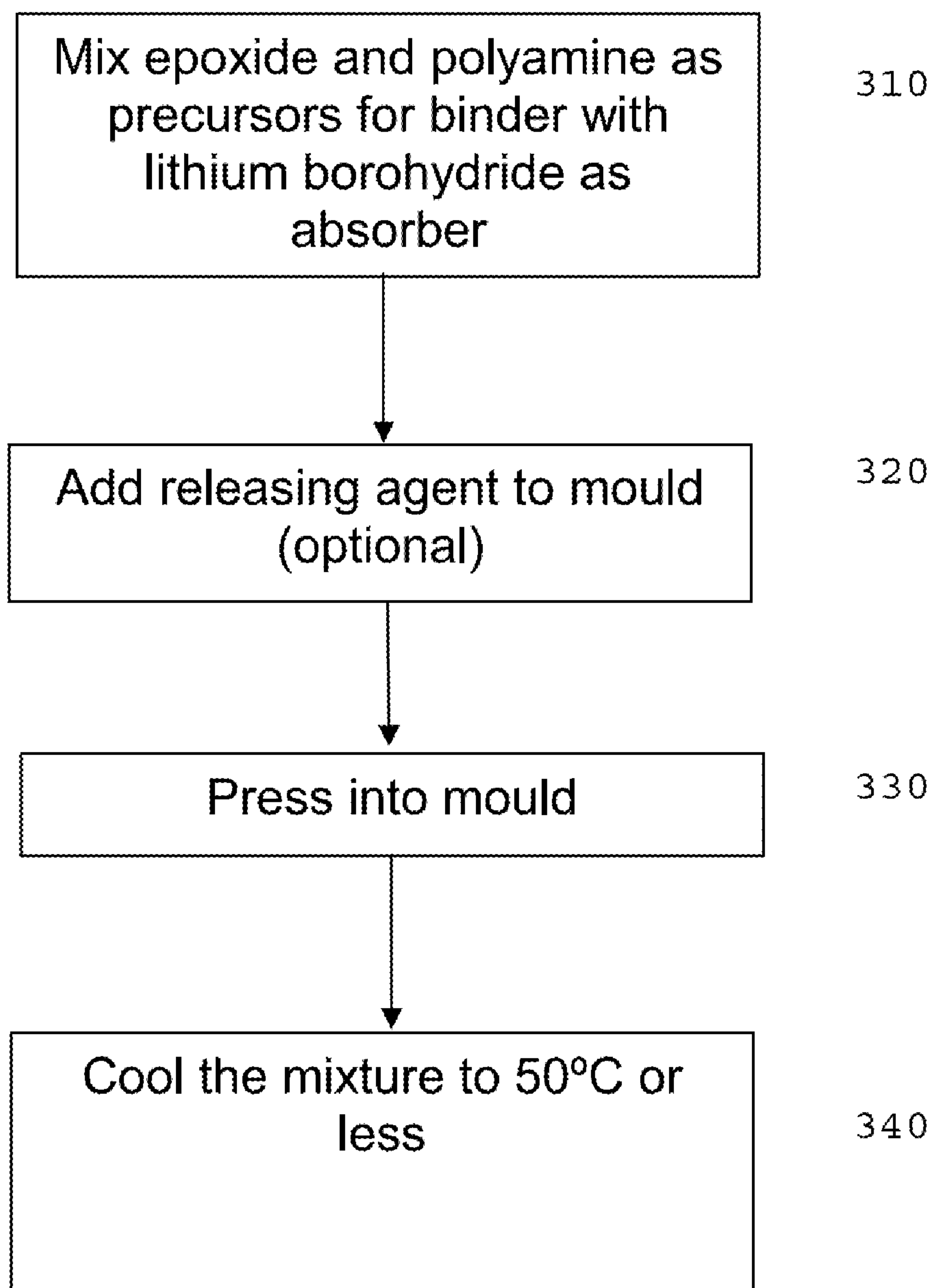


Figure 5

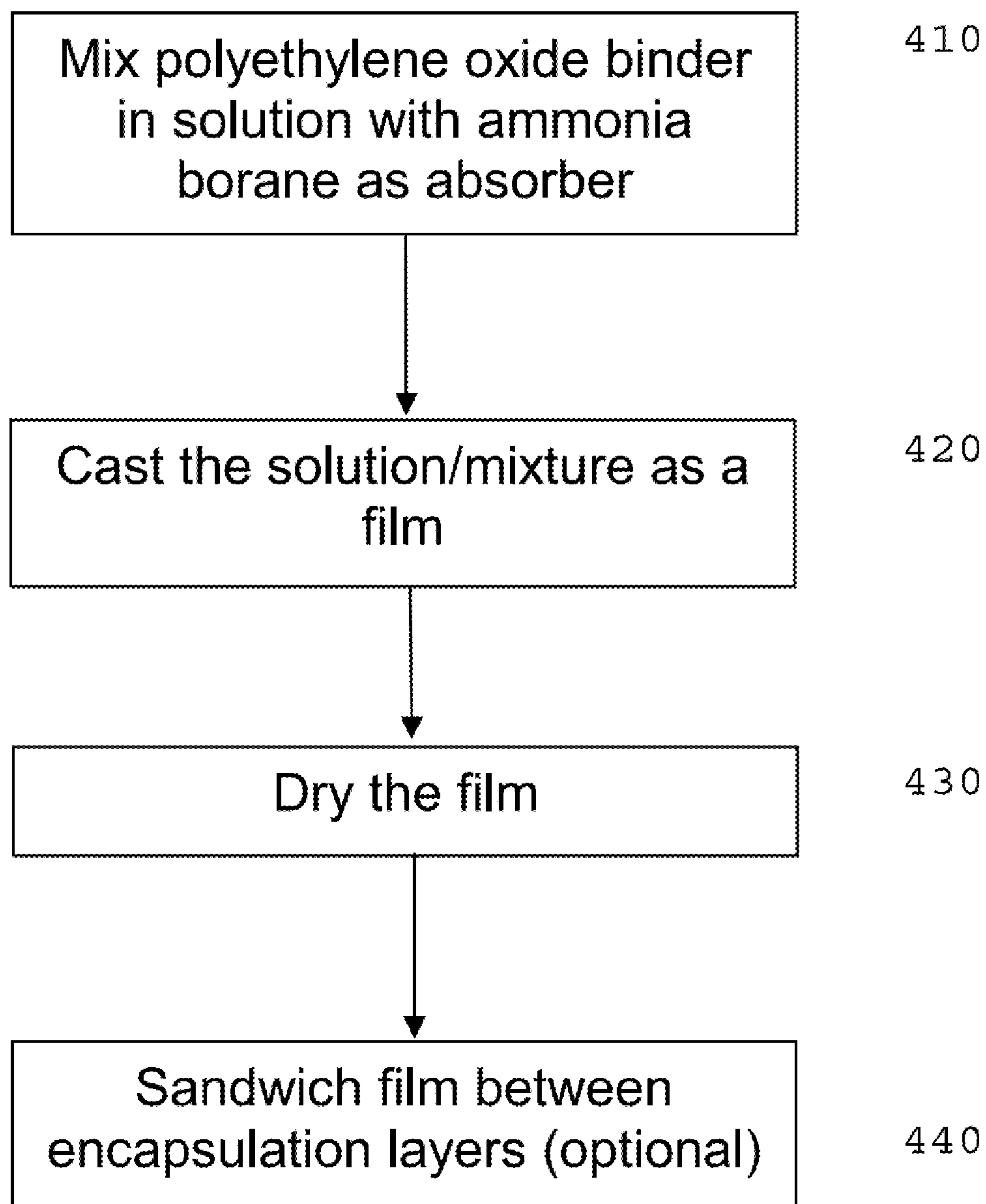


Figure 6

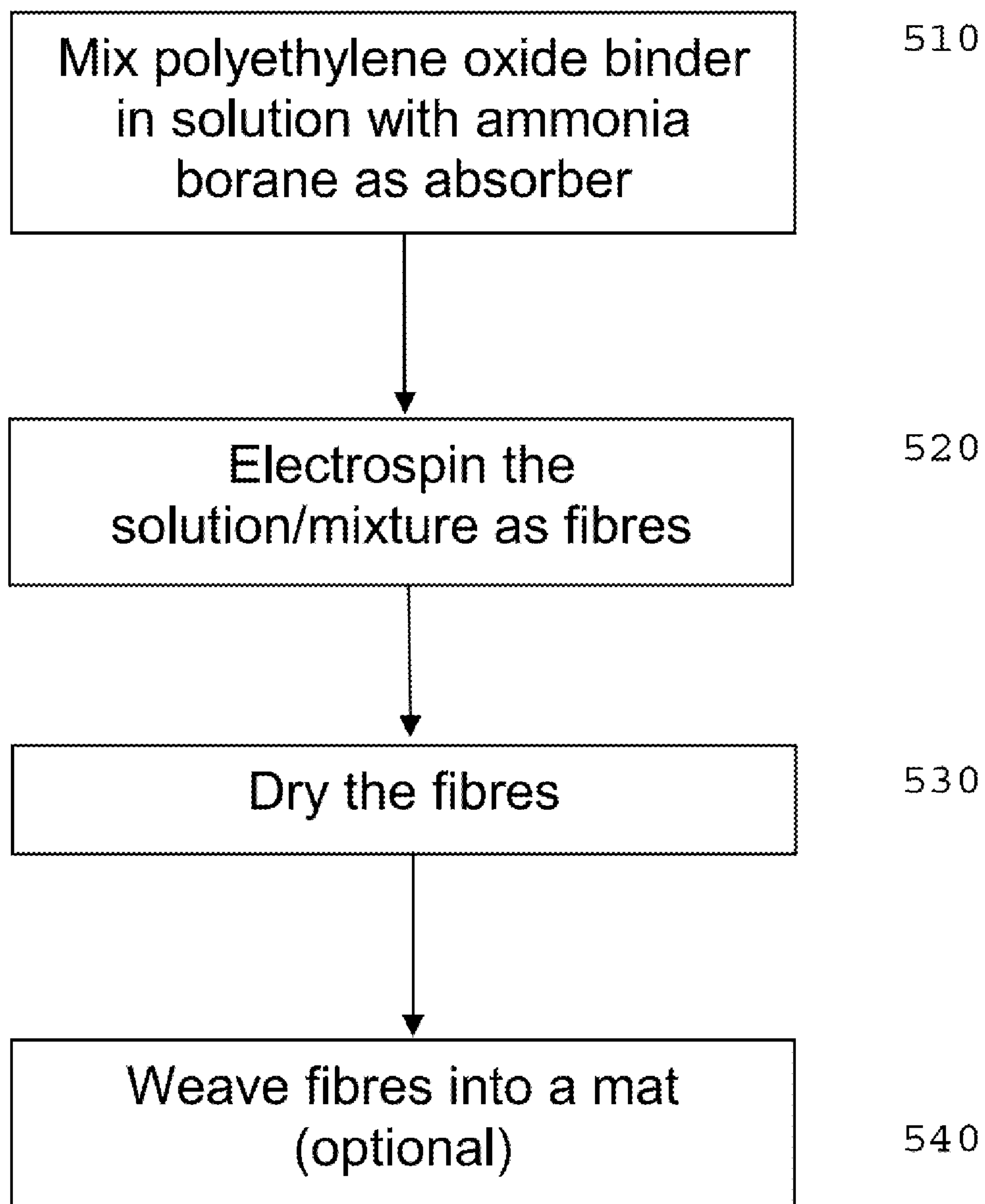


Figure 7

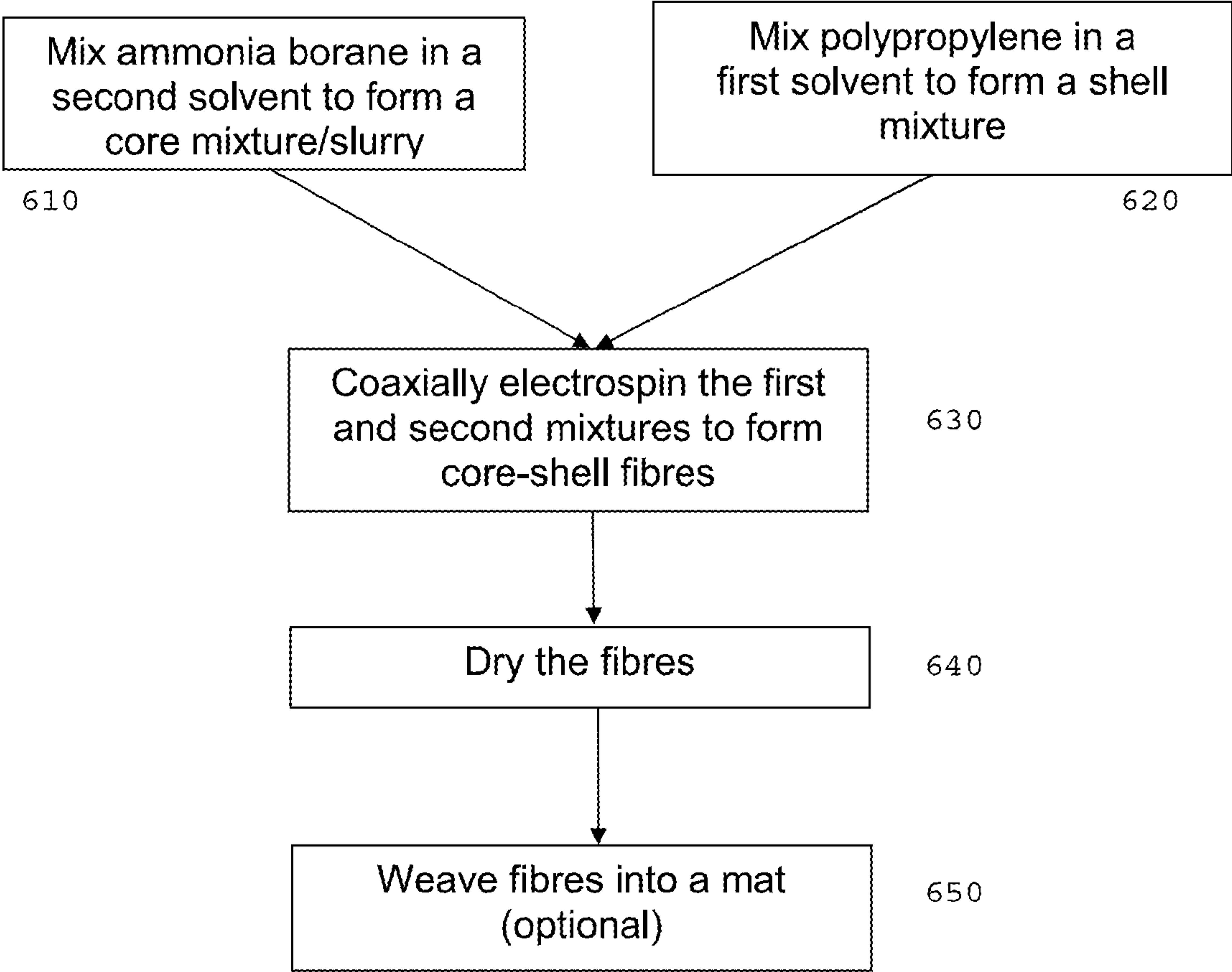


Figure 8

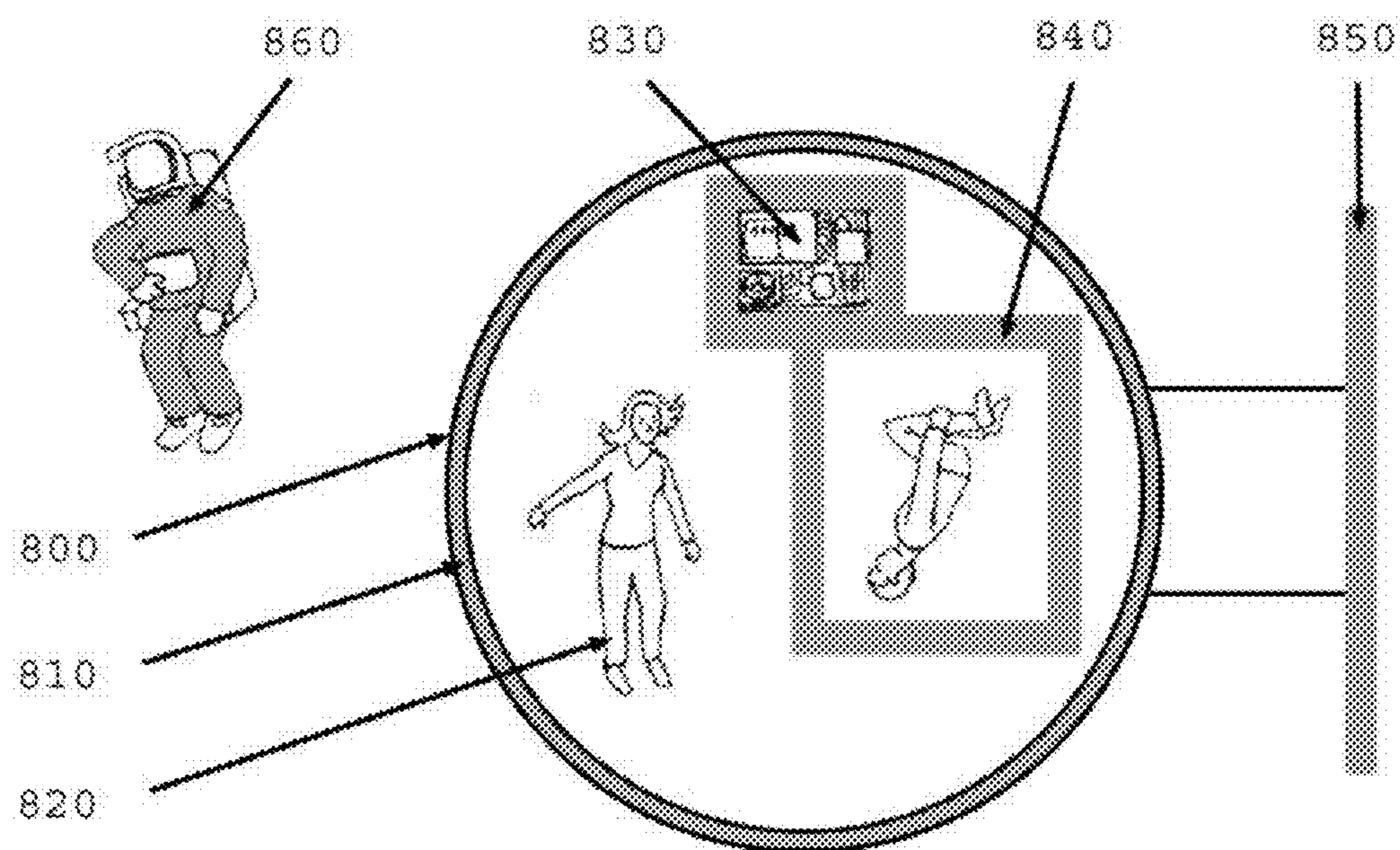


Figure 9

SPACECRAFT AND SPACESUIT SHIELD**TECHNICAL FIELD**

[0001] The present invention relates to space shielding and more particularly to shielding to reduce exposure to ionizing radiation in spacecraft, such as high energy electrons and protons. The present invention also relates to reducing exposure through spacesuits and to methods of manufacturing spacecraft and spacesuit shields.

BACKGROUND ART

[0002] Terrestrial radiation comes largely from nuclear decay and the remnants of cosmic and solar radiation that has interacted with the atmosphere. This radiation is made up of light charged particles with energies of around 1 to 2 MeV.

[0003] Radiation in space is made up of particles having much higher energies. Space radiation can be divided into three types. Firstly, solar particles are ejected from the sun in solar flares. The magnitude of these varies according to the sun's 11-year solar magnetic cycle. The particles are electrons and protons with energies typically in the range of hundreds of MeV to low GeV. The protons cause the majority of the damage. Extreme events are known as solar proton events (SPE). Galactic cosmic rays (GCR) are a second type of space radiation. These consist of energetic particles from events in deep space. The particles are protons, helium nuclei, and small numbers of heavier nuclei such as carbon and iron. These particles often have very high energy, for example in the range 1 to 20 GeV. A third type of radiation is that trapped by the earth's magnetic field. This trapped radiation is formed by some of the flux of protons and electrons coming from the sun. They are concentrated into two radiation bands called the Van Allen belts. The outer band consists mostly of electrons with energies in the range 0.1-10 MeV and the inner consists mostly of protons with energies up to 600 MeV.

[0004] In close earth orbit satellites benefit from the proximity of the earth and its magnetic field, but such satellites are outside the earth's atmosphere so they still receive significantly more radiation than on the surface of the earth. On earth space radiation produces an average dose of 0.4 mSv/year, whereas on the International Space Station this rises to 150 mSv/year. Deep space missions would subject humans to even greater doses, perhaps as high as 900 mSv/year.

[0005] Space radiation also has an impact on materials and electronics. Heavy ions, neutrons and protons can displace atoms in a semiconductor, introducing noise and error sources. The characteristics of capacitor dielectrics, metal resistor films, other passive electronic components and even wiring and cabling can be degraded by radiation over time.

[0006] It is also possible for high energy charged particles to alter the bits stored in computer memory. These are called single event upsets and can cause anything from a short-term denial of service to the loss of the satellite.

[0007] Most of the energy lost by an incoming particle in matter is through the interaction with electrons. So for space applications materials with the highest number of electrons per unit mass are best, which usually means materials with a high hydrogen content.

[0008] Very high energy irradiation can cause nuclear fragmentation in heavy elements such as aluminium, which is a common construction material for spacecraft. The materials that are the most efficient at shielding space radiation are those with the most electrons per unit mass. For these reasons,

hydrogen, and high hydrogen-containing materials, such as polyethylene, are preferred. Lead on the other hand is less efficient at absorbing energy per unit mass, and is more suited to terrestrial situations where volume, not mass, is more important.

[0009] Polyethylene, which is used on the International Space Station (ISS) as a radiation shield, contains only 14 wt % of hydrogen. Thus it is desirable to produce a material that has a higher hydrogen content per unit weight than polyethylene.

SUMMARY OF THE INVENTION

[0010] The present invention provides a spacecraft or spacesuit having a radiation shield, the shield comprising a hydrogen-containing material, compound or complex, and a polymer binder. The hydrogen containing compound or complex may also contain a neutron-absorbing element, such as boron or lithium. The radiation shield absorbs and dissipates the energy of high energy particles such as protons, electrons, helium nuclei and others described above to reduce their ability to cause damage, for example by ionization. The hydrogen-containing material is optionally also a neutron absorber. The types of spacecraft may be satellites or space stations. The invention is not however limited to these, but also includes any other types of spacecraft in which a reduction in exposure to the types of space radiation described above is desired.

[0011] The shield may comprise a first component which comprises a hydrogen-containing material or combination of materials, and a second component which is a polymer binder to hold the first component together thereby increasing its structural strength beyond that of the first component alone. The shield may be considered a composite.

[0012] The polymer binder may consist of single or multiple polymer types. The polymer binder may form a matrix through which the hydrogen-containing material is distributed to provide structural strength and rigidity.

[0013] The polymer binder may also confer other advantageous properties to the shield such as impact protection.

[0014] The polymer binder may encapsulate the hydrogen containing material. This is preferable if the material is sensitive to oxygen or moisture.

[0015] The shield may be formed as a bulk solid, as layers or films, or as fibres. A combination of forms may be used in the shield.

[0016] The binder may be a thermoplastic or thermosetting polymer.

[0017] If the binder is a thermoplastic polymer, it may be polyethylene, polypropylene, polyisobutylene, polybutadiene, poly (methylmethacrylate), polysulphone, polystyrene, poly (vinyl pyrrolidone), poly vinylidene fluoride, poly tetrafluoroethylene, poly ethylene oxide, poly vinyl acetate or polyester. It may be a co-polymer comprising two or more polymers. It may be poly (styrene-co-ethylene-ran-butadiene-styrene). If the binder is a thermosetting polymer, it may be polyepoxide, polyimide, polyamide, polyaramide or melamine formaldehyde.

[0018] The hydrogen-containing material is preferably an inorganic material. It may be a hydride.

[0019] The hydrogen containing material may be at least one of ammonia borane, ammoniumborohydride, methylammonium borohydride, lithium borohydride, an ammoniate of

lithium borohydride, a methyl amine borane, ammonia triborane, ammonium octahydrotriborane, and beryllium hydride.

[0020] The shield may comprise a fibre mat.

[0021] The present invention also provides a method of manufacturing a radiation shield for a spacecraft or spacesuit, comprising: mixing a polymer or polymer precursor binder with a hydrogen-containing compound or complex; shaping the mixture; and allowing the mixture to solidify; and incorporating the solid in a radiation shield for a spacecraft. Optionally, the hydrogen-containing compound may comprise a neutron absorber such as boron or lithium.

[0022] The polymer may be a thermoplastic or a thermosetting polymer.

[0023] The hydrogen containing material preferably has a hydrogen content greater than 14%, 15%, or 16% by weight. More preferably the hydrogen content is 17% or more by weight. The maximum hydrogen content for an inorganic complex may be around 25%, which is that for ammonium borohydride.

[0024] The hydrogen containing material has a higher hydrogen content by weight than the polymer binder. The hydrogen-containing material is preferably a solid at temperatures from -40 degrees C. to 150 degrees C. The step of solidifying may occur through polymerisation. For example, a polymer monomer and hydride may be mixed together and then a polymerisation initiator, accelerator or catalyst is added before the mixture is poured into a mould. Polymerisation produces heat and so cooling may be required. Polymerisation can also create radicals so it may be necessary to keep the mixture in an oxygen-free environment.

[0025] The production of bulk material may also be achieved using epoxy. For example, the two halves of the epoxy (resin and hardener) are mixed with the hydrogen-containing material just prior to pouring into a mould.

[0026] The method may further comprise the step of adding a surfactant or dispersant prior to, or during, the step of mixing. A surfactant helps materials or solvents to wet each other by reducing the surface tension between the two. A dispersant is a special kind of surfactant that helps colloid systems to be better dispersed by preventing settling or clumping. The dispersant may be a non-ionic surfactant. More particularly, the dispersant may be a poloxamer (also known by the trade name Pluronic®), sorbitan monopalmitate, ethylenediamine tetrakis(ethoxylate-block-propoxylate) tetrol average and/or poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol).

[0027] The method may further comprise adding a polymerisation catalyst prior to, or during, the step of mixing.

[0028] The step of shaping may comprise pressing the mixture into a mould. The mould may be airtight to prevent absorption of moisture as the mixture sets. The mixture in the mould is preferably cooled. The mixture may be cooled to maintain its temperature below the decomposition temperature of the hydrogen containing material. The mould may be lined with releasing agent. Some hydrogen containing materials will require little or no cooling, such as lithium borohydride which is stable to 200° C.

[0029] The method may be carried out in an environment of reduced oxygen and/or water vapour.

[0030] The step of mixing may comprise mixing the polymer or polymer precursor with a boron- and hydrogen-containing compound or complex in a shared solvent or solvent

blend to form a composite solution. A shared solvent is a solvent in which the polymer and hydrogen-containing material are soluble.

[0031] Melt casting may also be performed by pouring a liquid polymer into a mould with the hydrogen-containing material already mixed therein. Bulk solid material or sheets may be produced in this way.

[0032] The polymer precursor may be methyl methacrylate monomer, and the boron- and hydrogen-containing compound or complex may be ammonia borane.

[0033] The method may further comprise adding a catalyst prior to, or during, the step of mixing, wherein the catalyst is methyl ethyl ketone peroxide.

[0034] The polymer precursor may be epoxide, and the hydrogen containing compound or complex may be lithium borohydride.

[0035] The step of mixing may further comprise adding polyamine as a hardener and the resulting formation of polyepoxide as binder.

[0036] The step of shaping may comprise extruding a layer of solution onto a drum or belt and drying the layer to form a film or sheet.

[0037] The method may further comprise sandwiching the layer or film between sheets of oxygen- and/or moisture-impermeable polymer prior to the step of incorporating. Typically, the sheets may be high density polyethylene or polyisobutylene. In some embodiments the bulk or slab materials may also have oxygen- and/or moisture-impermeable polymer sheets bonded thereto.

[0038] The polymer may be polyethylene oxide or poly(vinyl pyrrolidone), the boron- and hydrogen-containing compound or complex may be ammonia borane, and the step of mixing may comprise mixing the polyethylene oxide or poly(vinyl pyrrolidone) and ammonia borane in water.

[0039] A further method of making the shield material is to use sintering of a mixture of powdered polymer and hydrogen-containing material. Sintering may take place at elevated pressures or temperatures.

[0040] The step of mixing may comprise mixing the polymer or polymer precursor with a boron- and hydrogen-containing compound or complex in a shared solvent or solvent blend to form a composite solution, and the step of shaping may comprise electrospinning the composite solution to form fibres. Single phase electrospinning of this kind can also be performed using a polymer melt. The polymer melt may be mixed with a powdered hydrogen-containing compound or complex, having a decomposition temperature higher than the polymer melt temperature.

[0041] The polymer may be polyethylene oxide or poly(vinyl pyrrolidone), the hydrogen-containing compound or complex may be ammonia borane, and the shared solvent may be water.

[0042] The present invention further comprises a method of manufacturing a radiation shield for a spacecraft, comprising: mixing a binder comprising a polymer or combination of polymers and/or polymer precursors in a first solvent, or combination of solvents, to form a shell solution, suspension or mixture; mixing a boron- and hydrogen-containing compound or complex in a second solvent or combination of solvents to form a core mixture; co-axially electrospinning the shell mixture through an outer, or annular, aperture of a coaxial nozzle, and the core mixture through a central, or core, aperture of a coaxial nozzle to form a fibre having a core formed solely or mostly of the boron- and hydrogen-contain-

ing compound or complex, surrounded by a shell formed of the polymer or combination of polymers mixed or formed from the polymer precursors; and incorporating the fibre in a radiation shield for a spacecraft.

[0043] Coaxial electrospinning can also be performed using a polymer melt as shell material, if a suitable high boiling-point fluid is used to dissolve or form a suspension with the hydrogen-containing material as a core mixture. Coaxial electrospinning may be performed at temperatures greater than 30 degrees C., with a shell mixture comprising a polymer solution or polymer melt and a core solution with suspended or dissolved hydrogen-containing material. This may include material with a decomposition temperature higher than the temperature of spinning.

[0044] The first (shell) and second (core) solvents are preferably immiscible.

[0045] The method may further comprise adding polymer to the core mixture.

[0046] The hydrogen-containing material may not be soluble, or may be only partly soluble, in the second solvent such that the core mixture is a colloid system or slurry.

[0047] The hydrogen-containing material may be ammonia borane and the binder may be polystyrene, polypropylene, poly vinylidene fluoride, polyisobutylene or polybutylene.

[0048] The shell mixture may be a solution, and the solvent may be toluene and/or xylene and/or N,N-dimethylformamide and/or N-dimethylacetamide and/or dimethyl sulphoxide. The core mixture may be a slurry of ammonia borane in water with poly (ethylene oxide).

BRIEF DESCRIPTION OF THE DRAWINGS

[0049] Embodiments of the present invention, along with aspects of the prior art, will now be described with reference to the accompanying drawings, of which:

[0050] FIGS. 1a to 1c are photos of the structure of materials made according to the present invention;

[0051] FIG. 2 is a flow chart showing steps in manufacturing a spacecraft with a shield according to the present invention;

[0052] FIG. 3 is a chart summarising exemplary manufacturing techniques and material examples;

[0053] FIG. 4 is a flow chart showing steps in manufacturing a material for a spacecraft shield according to a first detailed embodiment using casting of thermoplastics;

[0054] FIG. 5 is a flow chart showing steps in manufacturing a material for a spacecraft shield according to a second detailed embodiment using casting of thermosetting plastics;

[0055] FIG. 6 is a flow chart showing steps in manufacturing a material for a spacecraft shield according to a third specific embodiment using solution casting;

[0056] FIG. 7 is a flow chart showing steps in manufacturing a material for a spacecraft shield according to a fourth specific embodiment using single phase electrospinning;

[0057] FIG. 8 is a flow chart showing steps in manufacturing a material for a spacecraft shield according to a fifth specific embodiment using coaxial electrospinning; and

[0058] FIG. 9 is a schematic diagram of a spacecraft with shielding.

DETAILED DESCRIPTION

[0059] As mentioned above polyethylene is used in the International Space Station (ISS) as a radiation shield

because this is a stable non-toxic material with high hydrogen content. The amount of hydrogen by weight for polyethylene is 14%.

[0060] Some boron and hydrogen containing compounds have a hydrogen percentage by weight which is greater than for polyethylene. For example, ammonia borane has greater than 19% hydrogen by weight. Boron is also an excellent neutron absorber and as mentioned above, although space radiation does not contain neutrons, the nuclear fragmentation which occurs due to bombardment with high energy radiation does produce neutrons. Therefore, hydrogen- and boron-containing compounds such as ammonia borane provide better radiation shielding than polyethylene with the added advantage of also absorbing neutrons. Other solid materials with a high hydrogen content include those based on lithium, and beryllium (such as BeH₂). Lithium is also a good neutron absorber. The neutron-absorbing isotope of boron is boron-10 and the neutron-absorbing isotope of lithium is lithium-6. Using hydrogen-containing compounds or complexes enriched with these lighter isotopes confers both improved neutron absorption and a higher hydrogen weight content in the materials. Lithium has a neutron absorption coefficient of 70.5 barns which increases to 940 for lithium-6. Boron has a neutron absorption coefficient of 767 barns which increases to 3835 for boron-10.

[0061] Ammonia borane is a waxy solid with little structural strength. A number of other boron compounds with high hydrogen content are available but many do not have the required structural strength or stability alone for use in a radiation shield. Table 1 lists various hydrogen and boron compounds along with wt % of hydrogen and their stability.

TABLE 1

Compound	Formula	Hydrogen Content	Stability
Ammonia borane	NH ₃ BH ₃	19.6 wt %	Loses H slowly above 50° C. Melts & Degrades at 105° C.
Ammonium borohydride	NH ₄ BH ₄	24.5 wt %	Loses H above room temperature
Methylammonium borohydride	CH ₃ NH ₃ (BH ₄)	21.4 wt %	Loses H rapidly above 40° C.
Lithium borohydride	Li(BH ₄)	18.4 wt %	Stable to 300° C. Reacts with moisture and oxygen
Ammoniates of lithium borohydride	Li(NH ₃) _n BH ₄ (n = 1-3)	18.1 wt % (n = 1) 17.9 wt % (n = 2) 16.5 wt % (n = 3)	Loses H at 200° C. Melts at 57° C.
Methyl amine borane	(CH ₃) _n NH _{3-n} BH ₃ (n = 1-2)	18.1 wt % (n = 1) 17.9 wt % (n = 2)	
Ammonia triborane	NH ₃ B ₃ H ₇	17.7 wt %	

[0062] Some of the above materials are not sufficiently stable and must be stabilized before they will be useful as a shield material. Some of the materials are also sensitive to air and moisture and will require protection or encapsulation if exposed to atmosphere in processing or during use. The hydrogen content shown may be improved further by using materials enriched with boron-10 and/or lithium-6.

[0063] The present invention provides composite materials for use as a radiation shield in spacecraft and methods of manufacturing the material.

[0064] FIG. 2 is a flow chart showing a method of manufacturing a spacecraft having a shield. A hydrogen-containing compound or complex is used as an absorber of energy from high energy electrons, protons etc for the shield. This is mixed with a polymer, or a combination of polymers or polymer precursors. The polymers or polymer precursors may be a liquid or in a solution. This mixing step is shown at step 110. Thermosetting plastics and thermoplastics may be used as the polymer binder. Thermoplastics are formed when a catalyst is added to the monomer. Thermosetting plastics form through a mixture of a resin and a hardening agent. In both cases the chemical reaction will generate heat. The mixture of hydrogen-containing compound and binder should be actively cooled to below the hydrogen-containing compound decomposition temperature to prevent degradation and release of hydrogen.

[0065] After mixing the mixture will begin to set and any solvents used will begin to evaporate. The material should be shaped immediately after mixing, for example by pressing into a mould. The step of shaping is shown at 120 in FIG. 2. Material pressed into a mould, or cast, will produce slabs of shield material in which the hydrogen-containing compound is distributed throughout the binder and is held in a matrix of binder. The percentage by weight of the binder and hydrogen-containing compound is such that the majority of the slab is hydrogen-containing compound. To permit easy removal of the slab from the mould, the mould may be lined with a releasing agent. As well as slabs, other shapes of mould may be used to fabricate other shapes of shield material. After shaping the material, for example by pressing into a mould, the cooling of the mixture should continue, as indicated at step 130 in FIG. 2.

[0066] The binder provides structural rigidity while also protecting the hydrogen-containing compound from oxygen and moisture. This protection allows it to be handled during assembly on earth as well as allowing it to be used inside satellites or space stations. The rigidity provided by the binder also permits use as an independent structure outside, or spaced from, a spacecraft.

[0067] Once the mixture has cooled and set, the shield material can be incorporated in a spacecraft as shown at step 140 in FIG. 2.

[0068] In an alternative embodiment, the process of mixing hydrogen-containing compound and binder together and shaping the mixture may be performed simultaneously.

[0069] Examples of suitable polymers for the binder include poly(methyl methacrylate), polyethylene, polypropylene, polystyrene, poly vinylidene fluoride, polybutylene, polybutadiene, polyisobutylene polyester, and co-polymers comprising two or more of these. An example of a copolymer may be SEBS. These polymers are thermoplastics. Other examples of suitable polymers include polyepoxide, polyimide, polyamide, polyaramide and melamine formaldehyde. These are thermosetting plastics. Another alternative is polyethylene oxide or poly(vinyl pyrrolidone). Preferably molecular weights of greater than 1,000,000 (1M) and preferably 2M, 4M or 8M polyethylene oxide are used.

[0070] Depending on the compatibility of the hydride and monomer it may be necessary to use surfactants to reduce the surface tension between the absorber and polymer monomer in solution to keep the absorber in suspension until casting is

complete. For example, the absorber is likely to be a strongly polar molecule whereas the polymer may only have weak polarity. This may mean there is a difference in the types of solvent in which the absorber and polymer will be soluble. The surfactant improves the solubility of the absorber and/or polymer in the chosen solvent or solvent blend. The surfactant may be a non-ionic surfactant. Typically, the surfactant may be sorbitan monopalmitate, ethylenediamine tetrakis(ethoxylate-block-propoxylate) tetrol average and/or poly(ethylene glycol)-block-polypropylene glycol)-block-poly(ethylene glycol).

[0071] Alternative embodiments provide different shaping techniques to the above casting technique. A first alternative is to use solution casting. In this technique the hydrogen-containing compound and binder are dissolved in a common solvent or combination of solvents. The use of a single solvent in which the binder and hydrogen containing material are both soluble limits the choice of binders and solvents that can be used. After mixing the solution a thin layer of solution is extruded onto a drum or belt. As the solvent evaporates the hydrogen containing material adheres to the binder to form a solid solution or mixture. After evaporation a film of less than 500 μm thickness is produced, such as a film 10s or 100s of microns thick. Some of the hydrogen containing material mentioned above are sensitive to air or moisture. In such cases thin sheets of gas- and moisture-impermeable polymer, for example high-density polyethylene or polyisobutylene, are bonded to either side of the shield material. For shielding applications a large number of layers of the film will need to be stacked together to create the required thickness or areal density of absorber. Such a stacking process is a widely performed industrial process and is not expensive.

[0072] A second alternative is to use electrospinning to produce fibres. The produced fibres have micron- or sub-micron scale dimensions. Electrospinning is the process of extruding a solution or melt through a nozzle where a large electrostatic field causes a jet to issue from a Taylor cone. Solvents in the jet evaporate, or the melt solidifies, such that as the jet is pulled by the electrostatic field a fine fibre is produced.

[0073] Electrospinning can be performed in two ways; single phase electrospinning and co-axial electrospinning (also known as co-phase spinning or co-electrospinning). In single phase electrospinning the hydrogen containing material and binder are mixed in a common solvent in which both hydrogen containing material and binder are soluble, in a similar way to the solution cast method. The solution, or mixture, is fed to a nozzle with a single aperture to electrospin the fibre. Single phase electrospinning is not suitable for air- and moisture-sensitive hydrogen-containing absorber materials without further processing and encapsulation in a gas-impermeable layer. This is because the surface area of the fibres is large in comparison to bulk material so a large amount of absorber will be subjected to air or moisture.

[0074] Co-axial electrospinning uses a nozzle having a central aperture surrounded by an annular aperture to produce a fibre having a central core surrounded by an outer shell. The binder is dissolved in, or mixed with, a first solvent or combination of solvents to form a binder solution or mixture. The absorber is dissolved in, or mixed with a second solvent or combination of solvents to form an absorber solution or mixture. The two solvents, or combinations of solvents, are preferably immiscible. The binder mixture is supplied to the outer aperture of the nozzle, namely the annular aperture. The

absorber mixture is supplied to the inner aperture of the nozzle, namely the central core aperture. Electrospinning is then the same as for the single phase method. The absorber mixture may also include a small quantity of polymer to maintain stability during electrospinning and prevent collapse of the fibre as the solvents evaporate.

[0075] The fibres produced from single phase or co-axial electrospinning techniques can be packed into complex shapes to fit in the spacecraft. The fibres may be produced as a non-woven mat. The fibres are flexible, which allows them to be easily fitted into small and complex spaces, or can be made into moving or flexible parts such as in spacesuits or inflatable structures. Nevertheless, because the fibres pack with gaps between them, there will be some unused space between the fibres which will result in a reduction in absorber density compared to slab materials. A packing fraction for fibres is 0.8.

[0076] Another alternative is sintering in which fine powders of polymer and hydrogen-containing material are mixed together. The powder mixture is then sintered under pressure or heat to form the material into the required shape. Any heat applied during the sintering process should not result in a temperature being exceeded above which the hydrogen-containing material decomposes.

[0077] A summary of techniques with examples of compounds that may be used is shown in FIG. 3. The examples are not considered limiting and other techniques for those materials may be used. In the figure the following abbreviations are used:

[0078] PEO=polyethylene oxide

[0079] PP=polypropylene

[0080] PE=polyethylene

[0081] PMMA=poly methyl methacrylate

[0082] AB=ammonia borane

[0083] LB=lithium borohydride

[0084] The techniques listed in FIG. 3 can be summarised as:

[0085] i) sintering of a mixture of polymer and hydrogen containing material in powdered form;

[0086] ii.a) casting by solution or melt;

[0087] ii.b) casting by polymerisation, resin, or epoxy; and

[0088] iii) single phase and coaxial electrospinning.

[0089] We now describe examples of specific embodiments of the techniques.

First Example

[0090] As a first specific embodiment, we cast a shield slab having ammonia borane as the absorber in a poly(methyl methacrylate) binder. The steps of this method are shown in FIG. 4. At step 210 ammonia borane was mixed with the monomer, methyl methacrylate liquid using a shear mixer. A surfactant or more preferably a dispersant was added to the mixture to keep the ammonia borane in suspension for a sufficiently long time to allow the mixture to be handled and to solidify. This is shown at step 220. Since poly(methyl methacrylate) is a thermoplastic polymer a catalyst is used to initiate the polymerisation of the monomer. In this case methyl ethyl ketone peroxide (MEKP) was used as catalyst. At step 230 this is mixed in with the monomer and ammonia borane to produce a viscous slurry. The slurry is pressed into an airtight mould at step 240. Ammonia borane starts to lose hydrogen at 50° C. so the temperature of the contents of the mould are actively maintained below this, such as at 40° C. or

less, as shown at step 250. This example produces shield slabs of polymethyl methacrylate and ammonia borane (PMMA/AB in FIG. 3). The ratio of ammonia borane absorber to polymer binder is at least 80:20 wt % and even as high as 90:10 wt %.

[0091] A similar method may be used for resins or epoxies where the polymer or precursor is a liquid and is mixed with the hydrogen-containing material. An initiator can then be added to start hardening or polymerisation.

Second Example

[0092] FIG. 5 shows the steps of a second specific embodiment which uses lithium borohydride in epoxide. Epoxide was mixed with lithium borohydride and polyamine in an inert atmosphere at step 310. Epoxide is a thermosetting epoxy resin and the polyamine acts as hardener. The mould is lined with releasing agent at step 320. The mixture is pressed into the mould (step 330) and allowed to set.

Third Example

[0093] A third specific embodiment used the solution cast technique. The method steps are shown in FIG. 6. The materials used were polyethylene oxide (PEO) as binder and ammonia borane as absorber in water. 2,000,000 (2M) molecular weight polyethylene oxide at a concentration of around 3 wt % was used, and mixed (step 410) with ammonia borane at a concentration of around 8-10 wt % in water. The mixture was stirred and at the same time heated to 30-40° C. for several hours. The solution was then extruded on to a drum to form a film (step 420) and allowed to dry (step 430). The resultant film has a ratio of ammonia borane to polyethylene oxide of 70:30 wt %. This technique is shown in the summary of FIG. 3 as PEO/AB from solution casting. This composition has a preferred combination of structural strength and high hydrogen content, although higher ammonia borane contents by weight are possible, for example 80:20 wt % and 85:15 wt %. Ammonia borane is hygroscopic and absorbs moisture from the air. In the environment of space this will not be a problem. However, the spacecraft will be assembled, at least partly, on earth where moisture can be absorbed. The structure of the film may be impaired by the absorption of water, so the film may be encapsulated in polyethylene sheets bonded on either side of the film (step 440).

Fourth Example

[0094] FIG. 7 lists the method steps of a fourth specific embodiment. This embodiment used polyethylene oxide as binder and ammonia borane as absorber. The technique used to produce the shield material was single phase electrospinning. The materials used were similar to the solution cast technique. 2M molecular weight polyethylene oxide at a concentration of approximately 3 wt % was taken and mixed with ammonia borane at a concentration of 8-10 wt % in water, as shown at step 510. The mixture was stirred for several hours at room temperature. The resulting solution was electrospun at step 520 using conventional single phase spinning. The fibres usually dry during the electrospinning process, but may be dried further afterwards. Drying is listed at step 530. The produced fibres have a ratio of ammonia borane to polyethylene oxide of 70:30 wt % and this material is listed as PEO/AB single phase fibres in summary FIG. 3. This composition has a preferred combination of structural strength and high hydrogen content, although higher ammonia borane

contents by weight are possible, for example 80:20 wt % and 85:15 wt %. The produced fibres may be optionally moulded, collected or woven together to form a mat at step 540.

Fifth Example

[0095] A fifth specific embodiment produced core-shell fibres with ammonia borane encapsulated by polypropylene. The preparation technique was coaxial electrospinning. The steps of the method are shown schematically in FIG. 8. The core solution or mixture comprised a 10-15% solution of ammonia borane in N,N-dimethylformamide and is prepared at step 610. A small amount of polymer, polyethylene oxide, was added to the core solution to maintain stability during spinning. The shell solution or mixture comprised polypropylene of molecular weight 250,000 at concentrations of 10-15 wt % in cyclohexane or xylene mixed with 10-20 wt % acetone or N,N-dimethylformamide. This is prepared at step 620. At step 630, the core and shell solutions or mixture were coaxially electrospun to produce fibres having at least 40 wt %, and preferably at least 50 wt % ammonia borane content. As mentioned above for single phase electrospinning, the fibres dry during electrospinning or can be dried further afterwards, as shown at step 640. The practical limit for core:shell weight ratio appears to be 50:50 because of shell viscosity and flow rate requirements. This ratio of AB to PS produces only a 14 wt % material. To improve on this a polyolefin (PE, PP, possibly polyisobutylene, polybutylene and co-polymers thereof) shell is required. PP dissolves at elevated temperatures but can be spun at below <30° C. so 50:50 PP:AB fibres are possible without AB decomposition producing ~17 wt % H.

[0096] Optionally the fibres can be collected or woven to form mats of shield material. The five techniques described above are examples and numerous variations in the materials for the binder and hydrogen-containing absorber may be made without departing from the scope of the invention. Furthermore, the moulding and shaping techniques described may be interchanged to use other materials described.

[0097] In a final embodiment polyethylene as a current preferred choice for shield materials could be used as the binder according to the present invention. However, polyethylene (PE) is insoluble in most common solvents which makes its use in solution casting or electrospinning difficult. Polyethylene is normally manufactured using gaseous precursors and this also prevents use by the bulk casting technique. However, it is also possible to sinter the hydride and polyethylene into composite materials using high pressure techniques. For example, powdered lithium borohydride and polyethylene can be mixed together and subjected to high pressures in a press or through extrusion to make solid or flexible sheets, or shaped bulk materials.

[0098] This example embodiment may optionally include melting the polyethylene and carrying out melt casting as the decomposition temperature of lithium borohydride is above the polyethylene melting temperature. Polyethylene can be dissolved and electrospun in solvents such as cyclohexane or xylene at elevated temperatures, typically above 100 degrees C. Therefore a material may be made in a version of the fifth embodiment stated above, where single-phase or co-axial electrospinning at temperatures of 100 degrees C. or higher is used, and where a solution or suspension of the hydrogen-containing material with decomposition temperature higher than 100 C is combined with a polyethylene solution either as a single phase or as a core-shell composition. Other polymers

with a similar hydrogen content that could be processed in a version of this embodiment include polybutylene, polyisobutylene and polypropylene.

[0099] Table 2 below summarises some of the materials described above.

TABLE 2

	AB:polymer ratio	Hydrogen wt %	Density g/cm ³	Packing density	H density g/cm ³
PMMA + AB by casting	90/10	18%	0.81	1.0	15.0
PEO + AB by spin	80/20	17%	0.86	1.0	15.0
casting					
PEO-based fibres	80/20	17%	0.86	0.8	12.0
PP-based fibres	70/30	18%	0.83	1.0	14.8

[0100] FIG. 1 shows some shield materials manufactured according to the above techniques. FIG. 1a shows a fibre pellet. FIG. 1b shows PEO-AB spun fibres. FIG. 1c shows sheets of material.

[0101] After the shield material has been prepared the material is incorporated into a spacecraft for example in the manner shown in FIG. 8. The spacecraft 800 includes a region which can be occupied by humans 820 and also in which sensitive electronics 830 are housed. It is therefore required that this region be shielded from space radiation. A shield 810 is formed in the hull of the spacecraft to reduce the exposure of humans 820 to the radiation and also prevent degradation of the electronics 830 by the radiation. Part or all of the electronics 830 may also be provided with an extra layer of shielding to provide further radiation protection. Furthermore, the spacecraft may also have additional components that require shielding from radiation. For example, the spacecraft may include a "storm shelter" 840 inside the spacecraft. This would provide human occupants with a region of increased radiation protection such as may be useful in times of peak solar activity. The storm shelter would be exposed to air within the spacecraft and if a neutron absorbing element is present in the shield, the storm shelter would also protect against secondary radiation (nuclear fragmentation) from the hull. Additional components may be fitted to the outside of the spacecraft. Alternatively, because of the orientation of the spacecraft and the contents it carries it may only be necessary to shield one side of the spacecraft, namely that facing away from the earth and/or towards the sun. In such cases a shield 850 mounted externally from the spacecraft may be used. If the shield is manufactured from fibres or sheet-based materials described above, the shield may be folded up during launch and deployed after the spacecraft has reached the correct orbit. Furthermore, the flexibility of fibre-based materials makes them particularly useful for spacesuits and inflatable structures. Shield materials that are flexible may also be used in spacesuit 860.

[0102] The shield may be incorporated into or comprise a structural member or impact shield, for example a micrometeorite shield.

[0103] As well as using the bulk, film, fibre or mat-based shield materials individually it is also possible to combine the three types of materials. For example, in a given area a mixture of materials may be used to produce optimum shield packing in enclosed or complex spaces by using a mixture of

bulk and film or fibre shield materials. The materials described herein for use in spacecraft and spacesuits may also be used in other space objects in which radiation shielding is required, for example lunar or planetary habitation modules.

1. A spacecraft or spacesuit having a radiation shield, the shield comprising a hydrogen-containing material and a polymer binder.

2. The spacecraft or spacesuit of claim **1**, wherein the hydrogen-containing material has a hydrogen content greater than 14% by weight.

3. The spacecraft or spacesuit of claim **2**, wherein the hydrogen-containing material has a hydrogen content of 17% or more by weight.

4. The spacecraft or spacesuit of claim **1**, wherein the hydrogen-containing material has a higher hydrogen content by weight than the polymer binder.

5. The spacecraft or spacesuit of claim **1**, wherein the hydrogen-containing material is an inorganic compound.

6. The spacecraft or spacesuit of claim **1**, wherein the hydrogen-containing material is a hydride.

7. The spacecraft or spacesuit of claim **1**, wherein the hydrogen-containing material comprises borane and/or a borohydride.

8. The spacecraft or spacesuit of claim **1**, wherein the shield comprises a neutron absorber element.

9. The spacecraft or spacesuit of claim **8**, wherein the neutron absorber element has a neutron absorption cross-section of at least 50 barns

10. The spacecraft or spacesuit of claim **8**, wherein the neutron absorber element has a neutron absorption cross-section of at least 500 barns.

11. The spacecraft or spacesuit of claim **8**, wherein the hydrogen-containing material comprises the neutron absorber element.

12. The spacecraft or spacesuit of claim **8**, wherein the neutron absorber element is one or more of lithium and boron.

13. The spacecraft or spacesuit of claim **12**, wherein the neutron absorber is lithium isotopically enriched with lithium-6

14. The spacecraft or spacesuit of claim **12**, wherein the neutron absorber is boron isotopically enriched with boron-10.

15. The spacecraft or spacesuit of claim **1**, wherein the polymer binder forms a matrix through which the hydrogen-containing material is distributed.

16. The spacecraft or spacesuit of claim **1**, wherein the polymer binder encapsulates the hydrogen-containing material.

17. The spacecraft or spacesuit of claim **1**, wherein the shield is formed as a bulk solid.

18. The spacecraft or spacesuit of claim **1**, wherein the shield is formed of layers or films.

19. The spacecraft or spacesuit of claim **1**, wherein the shield is formed of fibres.

20. The spacecraft or spacesuit of claim **1**, wherein the binder is a thermoplastic or thermosetting polymer.

21. The spacecraft or spacesuit of claim **20**, wherein the binder is a thermoplastic polymer and is one or more of poly (methylmethacrylate), polyester, polyethylene, polybutylene, polyisobutylene, poly vinylidene fluoride, poly vinyl acetate, polybutadiene, polystyrene, polytetrafluoroethylene, polysulphone, or polypropylene.

22. The spacecraft or spacesuit of claim **20**, wherein the binder is a thermosetting polymer and is one or more of polyepoxide, polyimide, polyamide, polyaramide and melamine formaldehyde.

23. The spacecraft or spacesuit of claim **1**, wherein the polymer is polyethylene oxide and/or polyvinyl pyrrolidone.

24. The spacecraft or spacesuit of claim **1**, wherein the polymer is a co-polymer.

25. The spacecraft or spacesuit of claim **1**, wherein the hydrogen containing material is at least one of ammonia borane, ammonium borohydride, methylammonium borohydride, lithium borohydride, an ammoniate of lithium borohydride, a methyl amine borane, ammonia triborane, ammonium octahydrotriborate, and beryllium hydride.

26. The spacecraft or spacesuit of claim **1**, wherein the hydrogen-containing material and binder form layers having a thickness less than 500 μm .

27. The spacecraft or spacesuit of claim **1**, wherein the shield is a mat of fibres.

28. A material comprising a cast or sintered mixture of a polymer and a hydrogen containing material, wherein the polymer forms a matrix through which the hydrogen-containing material is distributed.

29. (canceled)

30. The material of claim **28**, wherein the polymer is one or more of polyethylene, polypropylene, polyisobutylene, polybutadiene, poly (methylmethacrylate), polysulphone, polystyrene, poly (vinyl pyrrolidone), poly vinylidene fluoride, poly tetrafluoroethylene, poly ethylene oxide, poly vinyl acetate, polyester, poly (styrene-co-ethylene-ran-butadiene-styrene), polyepoxide, polyimide, polyamide, polyaramide and melamine formaldehyde, or is a copolymer thereof.

31. Use of the material of claim **28** as a radiation shield of a spacecraft, spacesuit, or lunar or planetary habitation module.

32. A method of manufacturing a radiation shield for a spacecraft or spacesuit, comprising:

mixing a hydrogen-containing material with a polymer or polymer precursor;

shaping the mixture; and

solidifying the mixture such that the polymer forms a matrix through which the hydrogen-containing material is distributed; and

incorporating the solid in a radiation shield of a spacecraft or spacesuit.

33. The method of claim **32**, wherein the step of mixing comprises mixing the hydrogen-containing material and polymer or polymer precursor in a liquid to form a solution and/or suspension, and the step of shaping comprises electrospinning or electrospraying the solution and/or suspension to form fibres or beads.

34. The method of claim **33**, further comprising heating the mixture.

35. The method of claim **32**, wherein the hydrogen containing material has a decomposition temperature above the melting point of the polymer, the method further comprising melting the polymer and the step of shaping comprises electrospinning or electrospraying the mixture to form fibres or beads.

36. The method of claim **32**, wherein the step of mixing comprises mixing the hydrogen-containing material and polymer or polymer precursor in a liquid to form a solution and/or suspension, and the step of shaping comprises casting the solution and/or suspension to a film.

37. The method of claim **36**, further comprising sandwiching the film between two sheets of a gas-impermeable polymer.

38. The method of claim **32**, wherein the hydrogen-containing material has a decomposition temperature above the melting point of the polymer, the method further comprising melting the polymer and the step of shaping comprises casting the mixture in moulds or by rolling to form a sheet.

39. The method of claim **32**, wherein the step of mixing comprises mixing powdered hydrogen-containing material with powdered polymer, and the step of shaping comprises pressing or extruding the mixture, and further comprising sintering the mixture.

40. The method of claim **32**, wherein the polymer is a thermoplastic or thermosetting polymer.

41. The method of claim **32**, further comprising the step of adding a surfactant or dispersant prior to, or during, the step of mixing.

42. The method of claim **32**, further comprising adding a polymerisation catalyst prior to, or during, the step of mixing.

43. The method of claim **38**, wherein the mould is airtight.

44. The method of claim **38**, wherein the mixture in the mould is cooled.

45. The method of claim **44**, wherein the mixture is cooled to maintain its temperature at 50° C. or less.

46. The method of claim **44**, wherein the mixture is cooled to maintain its temperature at 40° C. or less.

47. The method of claim **38**, further comprising lining the mould with releasing agent.

48. The method of claim **32**, wherein the hydrogen-containing material has a hydrogen content greater than 14% by weight.

49. The method of claim **32**, wherein the hydrogen-containing material has a hydrogen content of 17% or more by weight.

50. The method of claim **32**, wherein the hydrogen-containing material has a higher hydrogen content by weight than the polymer binder.

51. The method of claim **32**, wherein the hydrogen-containing material is an inorganic compound.

52. The method of claim **32**, wherein the hydrogen-containing material is a hydride.

53. The method of claim **32**, wherein the hydrogen-containing material comprises borane and/or a borohydride.

54. The method of claim **32**, wherein the hydrogen-containing material comprises a neutron absorber element.

55. The method of claim **54**, wherein the neutron absorber element is one or more of lithium and boron.

56. The method of any of claim **32**, wherein the neutron absorber is lithium-6 and/or boron-10.

57. The method of claim **32**, wherein polymer is a thermoplastic or thermosetting polymer.

58. The method of claim **32**, wherein the polymer is one or more of polyethylene, polypropylene, polyisobutylene, polybutadiene, poly (methylmethacrylate), polysulphone, polystyrene, poly (vinyl pyrrolidone), poly vinylidene fluoride, poly tetrafluoroethylene, poly ethylene oxide, poly vinyl acetate, polyester, poly (styrene-co-ethylene-ran-butadiene-styrene), polyepoxide, polyimide, polyamide, polyaramide and melamine formaldehyde.

59. The method of claim **32**, wherein the polymer is a copolymer.

60. The method of claim **32**, wherein the hydrogen-containing material is selected from ammonia borane, ammonium borohydride, methylammonium borohydride, lithium borohydride, an ammoniate of lithium borohydride, a methyl amine borane, ammonia triborane, ammonium octahydrotriborate, and beryllium hydride.

61. A method of manufacturing a radiation shield for a spacecraft or spacesuit, comprising:

mixing a polymer or polymer precursor in a first solvent to form a shell mixture;

mixing a hydrogen-containing material in a second solvent to form a core mixture;

co-axial electrospinning the shell mixture through an outer aperture of a coaxial nozzle and the core mixture through a central aperture of a nozzle to form a fibre having a core formed of the hydrogen-containing material surrounded by a shell formed of the polymer from the shell mixture or formed from the polymer precursors therein; and

incorporating the fibre in a radiation shield for a spacecraft or spacesuit.

62. The method of claim **61**, wherein the first and second solvents are immiscible.

63. The method of claim **61**, further comprising adding polymer to the core mixture.

64. The method of claim **61**, wherein the step of mixing the hydrogen-containing material and second solvent forms a colloid or suspension.

65. The method of claim **61**, further comprising heating the mixture of polymer or polymer precursor and first solvent.

66. The method of claim **61**, wherein the hydrogen-containing material is an inorganic compound.

67. The method of claim **61**, wherein the hydrogen-containing material is a hydride.

68. The method of claim **61**, wherein the hydrogen-containing material has a higher hydrogen content by weight than the polymer binder.

69. The method of claim **61**, wherein the hydrogen-containing material comprises borane and/or a borohydride.

70. The method of claim **61**, wherein the hydrogen-containing material comprises one or more of lithium and boron.

71. The method of claim **61**, wherein the hydrogen-containing material comprises lithium-6 and/or boron-10.

72. The method of claim **61**, wherein the polymer is a thermoplastic or thermosetting polymer.

73. The method of claim **61**, wherein the polymer is one or more of polyethylene, polypropylene, polyisobutylene, polybutadiene, poly (methylmethacrylate), polysulphone, polystyrene, poly (vinyl pyrrolidone), poly vinylidene fluoride, poly tetrafluoroethylene, poly ethylene oxide, poly vinyl acetate, polyester, poly (styrene-co-ethylene-ran-butadiene-styrene), polyepoxide, polyimide, polyamide, polyaramide and melamine formaldehyde.

74. The method of claim **61**, wherein the polymer is a copolymer.

75. The method of claim **61**, wherein the hydrogen containing material is selected from ammonia borane, ammonium borohydride, methylammonium borohydride, lithium borohydride, an ammoniate of lithium borohydride, a methyl amine borane, ammonia triborane, ammonium octahydrotriborate, and beryllium hydride.