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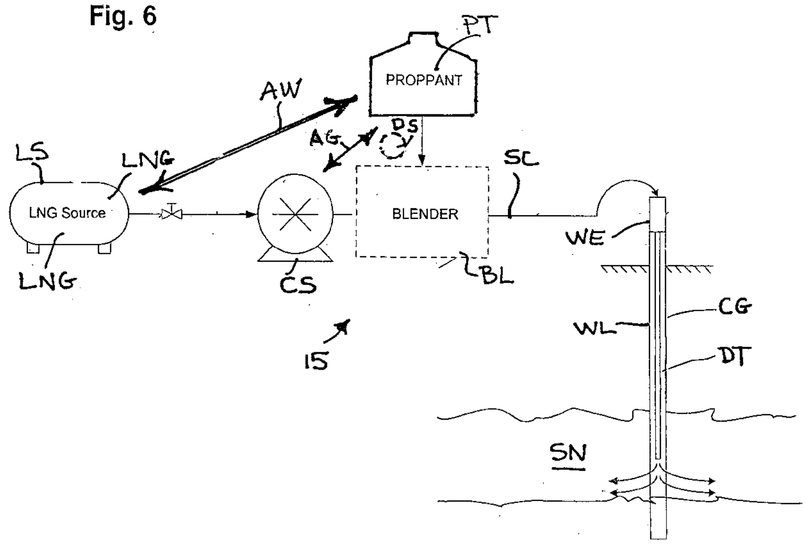
Fig. 6



(57) Abstract: New, unique and nonobvious : cryogenically treated proppants, materials, and nanomaterials; piggyback cryogenic systems; methods for cryogenic treatment; fracturing proppants; and fracturing methods. This abstract is provided to comply with the rules requiring an abstract which will allow a searcher or other reader to quickly ascertain the subject matter of the technical disclosure and is submitted with the understanding that it will not be used to interpret or limit the scope or meaning of the claims, 37 C.F.R. 1.72 (b).

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Cryogenic Treatments & Systems,
Materials Made With Them, & Methods For Using Them

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RELATED APPLICATIONS

The present invention and this application claim, under the Patent Laws, the benefit of and priority from pending U.S. Patent Applications Serial Nos. 61/852,196, 16 March 2013; and 61/962,063, 30 October 2013.

SUMMARY

The present invention, in certain aspects, discloses cryogenically treated materials, e.g., but not limited to, cryogenically treated proppants, cryogenically treated nanomaterials (e.g., nanotubes) and cryogenically treated materials useful in various well operations (e.g., drilling and production) and earth fracturing operations. In particular embodiments, cryogenically treated materials (e.g., materials, nanomaterials, and materials used as proppants) exhibit increased strength, improved shape characteristics, reduced friction, smoother surfaces, reduced fines production, increased sphericity, reduced and/or smoothed sites, areas, locations, or points for anchoring of undesirable materials to the surfaces of treated materials, improved thermal properties, improved electrical properties, improved electrical conductivity of conductive nanomaterials, improved electrical conductivity of conductive nanomaterials and of materials in or on proppants, and/or improved characteristics which enhance their various uses, e.g. as formation proppants. "Improved surface characteristics" include: improved shape characteristics, reduced friction, smoother surfaces, reduced fines production, increased sphericity, reduced and/or smoothed sites, areas, locations, or points for anchoring of undesirable materials to the surfaces of treated materials.

In some systems and methods according to the present invention, proppants (e.g, but not limited to sand and synthetic particles, e.g., but not limited to metal or ceramic particles, beads, and balls, hollow or not) are cryogenically treated to take them down to a selected cryogenic temperature, using a selected time for cooling and, in some aspects, a selected time resident at a cryogenic temperature, and then they are brought back to ambient temperature over a selected time period. Such treatments can increase the strength of the proppants. Such treatments can

improve the shape, e.g., but not limited to sphericity, of the proppants. Such treatments can improve the surface characteristics of the proppants and/or render surfaces smoother so that friction between proppants is reduced and proppant flow is enhanced. Such treatments can result in proppants from which relatively less fines are produced.

In addition to such treatments the proppants can be handled and/or subjected to a shaping system or structure (e.g., a mill, cryogenic flashing, cryogenic deburring, tumbler, grinder, hammermill, or shaker) and/or subjected to a flow regime and/or controlled turbulence and/or to flow passageways or conduits such that proppant shape and/or surface(s) are also improved. In particular aspects, proppants flow so that they impact a surface, member or target that breaks off, attrits, or abrades material, producing an enhanced-shape and/or enhanced-surface proppant. Any and all of these treatments and handlings can be repeated and proppants can be subjected to multiple cycles of them.

The present invention, in certain aspects, provides systems and methods for cryogenic treatment that use cryogenic environments or flow streams associated with existing apparatus, systems, containers, or equipment present at a location to provide cryogenic temperatures for the cryogenic treatment of proppants used in earth formation fracturing operations (or other material to be treated, whether used in fracturing or not). Such existing apparatus, collectively herein referred to as "existing cryogenic apparatus" or "ECA," includes, but is not limited to: liquid gas production apparatus; liquid gas transmission apparatus (e.g, transmission lines, conduits, pipe, pumps, and valves); liquid gas transport apparatus such as tanker trucks and tanker vessels; rail cars; air separation systems and plants; cryogenic pumps, cryogenic valves; cryogenic grinding systems; cryomill systems; cryoscrew systems; cryogenic screw conveyor systems; and liquid gas storage facilities, tanks, and vessels. Such liquid gases can include, but are not limited to, liquid air, liquid hydrogen, liquid inert gases, liquid nitrogen, and liquid helium at their corresponding cryogenic temperatures. Such existing apparatus is included in "piggyback" systems according to the present invention.

Existing systems, devices, equipment, and apparatus ("piggyback systems") useful in systems and methods according to the present invention which provide material at suitable cryogenic temperatures have various uses and are present at a variety of locations such as, among others, at, nearby, or remote from: well drilling sites, existing well production sites, processing facilites for producing and/or processing crude oil, processing facilities for producing and/or processing natural gas, processing facilities for drilling fluids, refining systems and/or refineries, systems for injection of liquid gas and/or liquid gas in a mixture, fracturing fluid preparation systems and/or facilities, injection fluid preparation systems and/or facilities, liquid gas plants, collection facilities for collecting liquid gas, pipelines, and facilities for transmitting liquid gas; e.g., but not limited to, systems and methods using or associated with cryogenic fluids, e.g, as in U.S. Patents 8,631,872; 8,627,889; 8,622,135; 8,596,362; 8,596,349; 8,584,755; 8,571,843; 8,540,019; 8,522,875; 8,496,057; 8,496,056; 5,967,233; 5,470,823; 5,310,003; 4,665,990; 4,566,539; 4,044,833; 3,768,564; and in U.S. Published Patent Applications 2011/0127033; 2010/0101795; 2007/0240880.

The cryogenic temperature provided by an existing system, etc., is accessed directly or indirectly in systems and methods according to the present invention to treat proppants or other materials to be treated. In certain embodiments, proppants (and/or other material to be treated) come in direct contact with fluid at a cryogenic temperature (e.g., in fluid flow stream or by immersion) and the proppants (and/or other material to be treated) are removed from, separated from, screened from, extracted from, or filtered from the fluid after cryogenic treatment, or, vice versa, the fluid is removed from, etc. the proppants (and/or other material). Any suitable known separation systems or apparatus may be used, e.g., but not limited to, filtration, magnetic separation, screening, centrifugal separation, density differential separation, and vortex or upflow separation. The use of an existing system which has, uses or contains a cryogenic material or cryogenic apparatus for providing a cryogenic treating temperature, improved according to the present invention is referred to herein as a "piggyback system" and the use of such for cryogenically treating proppants, proppant component(s), coatings, nanomaterial, nanotubes, composites, matrices, fabrics, fibers, webs, felts, laminates, ceramics, or other material is referred to as "piggybacking." "Other material" which may be cryogenically treated according to the present invention may include any material or thing disclosed herein which is cryogenically treated as well as those materials and things listed in the previous sentence.

The present invention, in certain aspects, provides systems and methods for cryogenic treatment of proppants and/or other materials to be treated which include their own dedicated cryogenic system. Such systems and methods can rely on the dedicated system alone or they can be used in conjunction with an existing cryogenic apparatus, on site or remote therefrom.

In certain embodiments, proppants (and/or other material to be treated) is subjected to cryogenic temperatures provided by intermediate structure or apparatus between fluid at cryogenic temperature and the proppants. For example, fluid at cryogenic temperature flows in a first conduit within a second conduit and the proppants and/or other material flows in the second conduit; with the cryogenic fluid of the first circuit providing cooling for the contents of the second conduit so that the proppants and/or other material is cryogenically treated; or, vice versa, the proppants are in the first conduit and the fluid flows in the second conduit. In other aspects, the two conduits are adjacent each other. In such systems, the proppants can flow or be introduced batchwise, the fluid can flow or be introduced batchwise, or both fluid and proppants can flow continuously (in the same direction or counter to each other). In other embodiments, a heat exchange system with an appropriate heat exchange apparatus or apparatuses is used to provide cryogenic cooling of proppants and/or other material by a thermal exchange with fluid at a cryogenic temperature in a batch or continuous flow regime.

In certain embodiments of the present invention, all or part of a cryogenic fluid flow stream or cryogenic fluid mass (e.g., in a vessel) is diverted or rerouted to a system and method according to the present invention to provide the cryogenic temperature, directly or indirectly, for the cryogenic treatment of proppants and/or of other material to be treated according to the present invention. In one particular aspect, a portion of a primary stream of flowing liquid gas is fed to an apparatus for cryogenic treatment of proppants and/or other material to be treated and then this portion is fed back to and rejoins the primary stream. Optionally, the portion is not fed back to the primary stream.

In any system and method according to the present invention, a suitable cryogenic treatment method or protocol is employed for the particular material of which a proppant is made (or for a particular material that is to be cryogenically treated). These suitable treatment methods include known cryogenic treatment methods and protocols for known materials, such as, but not limited to, known cryogenic treatments of metal, steel, plastics, polymers, ceramics, minerals, composites, fibers, carbon material (e.g., fibers, sheets, or layers), and glass. These suitable treatment methods can also include any suitable known heating method or protocol for raising a material from a cryogenic temperature.

In certain aspects in particular embodiments of the present invention, cryogenic treatment methods or protocols are employed to effect desired microcracking of all of or of part of a proppant and/or other material to be treated (e.g., but not limited to a proppant core, a proppant component, proppant reinforcement e.g. fibers and/or nanomaterial and/or nanotubes, proppant coating or coatings, or proppant layer or layers), which in some aspects provides: desired stress-relieving microcracking; desired damage-inducing microcracking; desired shatter-inducing or destruction-inducing microcracking; desired weakening of a proppant or of other material; or desired fluid-flow or permeability-increasing microcracking. Desired microcracking can be located throughout, in only part of, at or near a surface of, or in only a particular area of a proppant (or other material). Desired cracking and/or microcracking can be effected -with a cool down scheme, ramp up to room temperature scheme, or both - to provide a fluid flow path or flow paths through a proppant or material. In certain aspects, a "fluid flow" proppant is provided with fluid flow path(s) for fluid to flow through the proppant, e.g., water, fracking fluid, drilling fluid, oil, natural gas, or fluid hydrocarbons.

The present invention provides, in certain aspects, systems and methods for the cryogenic treatment of component(s) of proppants and then for the assembling and/or making of the final proppant product that includes the cryogenically-treated component(s). In one particular aspect, cryogenically-treated nanomaterial is used in part of (core, layer, and/or coating) such a proppant, e.g., but not limited to cryogenically-treated carbon nanotubes. In one particular aspect, a core or central material of a proppant is cryogenically-treated (to achieve any of the goals stated herein, or possible combination of the), and then a non-cryogenically-treated layer or coating is applied to the treated core or central material; or vice versa the core is not treated and a layer or coating is treated.

In any system herein according to the present embodiment, non-cryogenic apparatus and systems may be used to lower the temperature of a proppant or of other material to reduce the cooling load demands on a cryogenic system - either an existing system or a dedicated system. In certain particular aspects, the non-cryogenic apparatus is a refrigeration plant.

The present invention, in certain aspects, provides systems for the cryogenic treatment of proppants, which systems use cryogenic temperatures associated with liquefied gas, e.g. such gas used as a fracturing fluid to stimulate production of hydrocarbons from and/or injectability of fluids into subterranean formations. The liquefied gas may be any suitable liquefiable gas, e.g., but not limited to, certain inert gases, e.g., nitrogen or helium, and also including liquefied natural gas (which can include any suitable gas component of natural gas, e.g., but not limited to methane).

All or a portion of liquefied gas used in the process, before it is introduced into a wellbore and earth to effect formation fracturing or during such introduction (with suitable conditions and parameters to cryogenically treat the proppants rather than existing methods which ignore this option), is flowed to contact proppants or to pass through a heat exchange apparatus so that the proppants are exposed to cryogenic temperatures for sufficient time to cryogenically treat the proppants. For fracturing, the liquefied gas and the proppants are then pumped into the wellbore. Optionally, if the temperature of the gas is too low to properly treat the proppants, depending on the size and/or on the material from which the proppants are made, the temperature is raised using appropriate apparatus so that the proppants are treated at a suitable temperature.

In certain aspects, the present invention provides methods of stimulating a subterranean formation to increase hydrocarbon production from the subterranean formation (the stimulating including but not limited to fracturing), the method including: cryogenically treating proppants for use in the stimulation operation, using an existing cryogenic apparatus and/or a dedicated cryogenic apparatus, in which when used the existing cryogenic apparatus includes apparatus for providing, processing, transmitting, and/or removing liquefied natural gas used in the stimulation operation; drawing the liquefied natural gas from a liquefied natural gas source; blending proppants with the liquefied natural gas and pumping the liquefied natural gas with the cryogenically-treated proppants at a pressure and a flow rate high enough to induce fracturing of the subterranean formation; and conducting the natural gas into the subterranean formation (e.g., part of an oil well, part of a gas well, a coal bed seam, a storage cavern or permeable strata, an aquifer a tar sand, or shale).

It is within the scope of the present invention to reduce the amounts of unwanted "fines" from proppants by treating according to methods of the present invention. When cryogenic treatment results in a proppant that is more spherical, with a smoother surface, a proppant with less pronounced projections, and/or a proppant with a smoother surface, fines from an amount of such proppants can be reduced and/or undesirable anchoring of material to a surface is reduced. This is also true of other material to be treated when such results are produced by cryogenic treatment.

In all drawings (except photomicrographs), items, proppants, coating, layers, reinforcing agents, and parts of proppants are not shown to scale, unless otherwise stated. Items and proppants shown in crosssection may have any suitable shape. Proppants shown in crosssection in particular embodiments have a generally spherical shape or they may have any suitable shape, and may be e.g., solid, hollow, or have material therein or be fluid-filled.

DESCRIPTION OF THE VIEWS OF THE DRAWINGS

Fig. 1A is a schematic view of a system according to the present invention.

Fig. 1B is a schematic view of a system according to the present invention.

Fig. 1C is a schematic view of a system according to the present invention.

Fig. 2 is a schematic view of a system according to the present invention.

Fig. 3 is a schematic view of a system according to the present invention.

Fig. 4A is a schematic view of a system according to the present invention.

Fig. 4B is a schematic view of a system according to the present invention.

Fig. 5 is a schematic view of a system according to the present invention.

Fig. 6 is a schematic view of a system according to the present invention.

Fig. 7 is a schematic view of a system according to the present invention.

Fig. 8 is a schematic view of a system according to the present invention.

Fig.9 is a schematic view of a system according to the present invention.

Fig. 10 is a crosssection view of a proppant according to the present invention.

Fig. 11 is a crosssection view of a porppant according to the present invention.

Fig. 12A is a crosssection view of a proppant according to the present invention.

Fig. 12B is a crosssection view of a porppant according to the present invention.

Fig. 12C is a crosssection view of a proppant according to the present invention.

Fig. 12D is a crosssection view of a porppant according to the present invention.

Fig. 13A is a crosssection view of a proppant according to the present invention.

Fig. 13B is a crosssection view of a porppant according to the present invention.

Fig. 14A is a crosssection view of a proppant according to the present invention.

Fig. 14B is a crosssection view of a porppant according to the present invention.

Fig. 15 is a schematic view of a system and process according to the present invention.

Fig. 16A is a scanning electron microscope picture of commercially available untreated sand usable as a proppant, at X50 magnification.

Fig. 16B is a scanning electron microscope picture of commercially available untreated sand usable as a proppant, at X50 magnification.

Fig. 17A is a scanning electron microscope picture at X1000 magnification, of sand as in Figs. 16A and 16B.

Fig. 17B is a scanning electron microscope picture at X5000 magnification, of sand as in Figs. 16A and 16B.

Fig. 17C is a scanning electron microscope picture at X5000 magnification, of sand as in Figs. 16A and 16B.

Fig. 18A is a scanning electron microscope picture of cryogenically treated sand according to the present invention usable as a proppant, at X50 magnification. The sand before treating was sand as in Figs. 16A-17C

Fig. 18B is a scanning electron microscope picture of cryogenically treated sand according to the present invention usable as a proppant, at X50 magnification. The sand before treating was sand as in Figs. 16A-17C

Fig. 18C is a scanning electron microscope picture at X50 magnification of cryogenically treated sand according to the present invention. The sand before treating was sand as in Figs. 16A-17C

Fig. 19A is a scanning electron microscope picture at X5000 magnification of sand as in Figs. 18A - 18C.

Fig. 19B is a scanning electron microscope picture at X1000 magnification of sand as in Figs. 18A - 18C.

Fig. 20A is a scanning electron microscope picture of commercially available untreated ceramic proppants, at X50 magnification.

Fig. 20B is a scanning electron microscope picture at X1000 magnification of the ceramic proppants of Figs. 20A.

Fig. 20C is a scanning electron microscope picture at X5000 magnification of the ceramic proppants of Figs. 20A.

Fig. 21A is a scanning electron microscope picture at X50 maghnification of the ceramic proppants of Fig. 20A after cryogenic treatment according to an embodiment of the present invention.

Fig. 21B is a scanning electron microscope picture at X1000 magnification of the ceramic proppants of Figs. 21A.

Fig. 21C is a scanning electron microscope picture at X5000 magnification of the ceramic proppants of Figs. 21A.

Fig. 22 is a schematic perspective view of a composite according to the present invention.

Fig. 23 is a crosssection schematic view of a composite according to the present invention.

Fig. 24A is a schematic view of a fabric according to the present invention.

Fig. 24B is a schematic view of a fabric according to the present invention.

Fig. 24C is a schematic view of a fabric according to the present invention.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

As shown in Fig. 1A, a system 10 according to the present invention has an existing cryogenic apparatus CAa with a space or area Sa (or associated with such a space or area) in a vessel, conduit, or container Va which contains fluid Fa which is at a cryogenic temperature due to cryogenic fluid in and/or flowing through the apparatus CAa. In one particular aspect, the fluid Fa is itself cryogenic fluid (e.g., liquid gas). The cryogenic temperature is at a level suitable for cryogenic treatment of proppants Pa introduced into the space Sa from a source of proppants Ra. Either the fluid Fa (e.g., through conduit Cf), the proppants Pa (e.g., through conduit Cp), or both are removed from the space Sa for recovery of the treated proppants.

As shown in Fig. 1B, a system 11 according to the present invention has an existing cryogenic apparatus CAb with a space or area Sb (or associated with such a space or area) in a vessel, conduit, or container which contains fluid Fb which is at a cryogenic temperature due to cryogenic fluid in and/or flowing through the apparatus CAb. In one particular aspect, the fluid Fb is itself cryogenic fluid (e.g., liquid gas). The cryogenic temperature is at a level suitable for cryogenic treatment of proppants Pb in an adjacent structure Tb from a source of proppants (not shown). The fluid Fb cools the proppants Pb by heat transfer between the existing cryogenic apparatus CAb and the adjacent structure Tb. The proppants Pb are sufficiently cooled for a sufficient time period to cryogenically treat the proppants Pb as desired.

As shown in Fig. 1C, a system 12 according to the present invention has an existing cryogenic apparatus CAc with a space or area Sc (or associated with such a space or area) in a vessel, conduit, or container which contains fluid Fc which is at a cryogenic temperature due to cryogenic fluid in and/or flowing through the apparatus CAc. In one particular aspect, the fluid Fc is itself cryogenic fluid (e.g., liquid gas). The cryogenic temperature is at a level suitable for cryogenic treatment of proppants Pc in a structure Tc from a source of proppants (not shown). A heat exchange apparatus Hc (or apparatuses) is disposed between the apparatus CAc and the structure Tc. The heat exchange apparatus Hc provides cryogenic cooling, derived from the fluid Fc, for the proppants Pc in the structure Tc.

It is within the scope of the present invention for a fluid at cryogenic temperature which is flowing to provide the cold-fluid basis for the cooling of proppants which are either static, are themselves flowing within the fluid itself, or are flowing in an adjacent structure (e.g., a pipe, conduit, heat exchange apparatus, or tubular). As shown in Fig. 2, in a system

13 according to the present invention, fluid Fd at cryogenic temperature is flowing in a conduit Cd of an existing cryogenic apparatus (not shown). In an adjacent flow line Ce, proppants Pe are flowing. The fluid Fd cools the proppants Pe (or, optionally, cools fluid Fp in which the proppants are entrained, thereby cooling the proppants Pe). Optionally, the apparatus with the fluid Fd is a dedicated apparatus used for cryogenically treating the proppants. In any suitable system and method herein described for proppants, other material may be treated instead of proppants.

It is within the scope of the present invention to use a portion of a stream of fluid at a desired cryogenic temperature for cryogenically treating proppants. As shown in Fig. 3, in a system 14 according to the present invention, a portion Na of a stream of fluid Ff at a cryogenic temperature is taken off and introduced to a structure Sf to cryogenically treat proppants Pf therein. The fluid Ff may be evacuated from the structure Sf in a stream Mf and, optionally, returned to the stream of fluid Ff. The stream Ff may be from or a component of an existing cryogenic apparatus or it may be from or a part of a dedicated apparatus. As for any treatment according to the present invention, this may be a batch or continuous process with proppant flow into and out of the structure Sf.

As shown in Fig. 4A, proppants Pg are cryogenically treated in a cryogenic fluid Fg in a dedicated apparatus Dg. As shown in Fig. 4B, proppants Ph are cryogenically treated in a structure Sg via a heat exchanger Hg which provides a cryogenic temperature derived from cryogenic fluid Fi in a dedicated apparatus Di. Nanotubes or carbon nanotubes may be substituted for the proppants of Figs. 1A - 4B.

The present invention includes feeding cryogenically treated proppants into a flow stream introduced into a tubular, a wellbore, and/or an earth formation; e.g., but not limited to, a flow stream of injection or fracturing fluid, e.g., but not limited to, a flow stream of liquid gas, liquid helium or liquid nitrogen. As shown in Fig. 5, proppants Pj, which have previously been cryogenically treated (e.g., by any system herein and/or according to any method or process herein), are fed into a stream Fj of fluid, e.g., but not limited to fracturing fluid, for introduction into a well and/or into an earth formation.

For any system and method described above or below, a suitable treatment regime, process, cycle, program, or protocol is followed based on the material of the proppants (or material other than proppants, which other material may be subjected to any of the appropriate treatments disclosed or referred to herein; the other material including, but not limited to, nanotubes, including but not limited to carbon nanobtubes-the nanotubes used in or on a proppant, or not-said such other material including such nanotubes and such carbon nanotubes referred to herein as "other material that may be treated") being treated and the goal of the treatment, with a desired treatment temperature, desired treatment times (ramp-up and ramp-down, and resident times), and, if desired, desired cool-down cycle(s) and heat-up cycle(s), so that the proppants or material in or on them are treated as desired. Known cryogenic treatment regimes, etc. are used for the treatment of known materials that are susceptible to cryogenic treatment, including known materials used in proppants or other material that may be treated (although such treatment of proppants or of nanomaterial is not known or suggested by prior knowledge, nor obvious in view thereof). Certain known regimes, etc. are known which produce some effects that, in the past, have been avoided and have in the past been seen as undesirable, but which according to the present invention are taken advantage of, although the prior art taught that these effects are disadvantages, to be avoided, and present problems, e.g., destructive and /or deleterious microcracking and creation of undesirable fluid flow paths that are to be avoided.

Fig. 6 is a schematic illustration of a system 15 for fracturing a well in accordance with an embodiment of the present invention in which liquefied natural gas LNG and cryogenically treated proppants PT are pumped into a well WL. In one aspect, the proppants PT are blended with the liquefied natural gas prior to pumping the liquefied natural gas into the well. Optionally, the liquefied natural gas is heated prior to entry into the well. Liquefied methane may be used instead of, or in combination with, liquefied natural gas, and this is included n the scope of "LNG".

The proppants PT are cryogenically treated using the liquefied natural gas - indicated by the arrow AW - and the treatment may be as in any embodiment of the present invention, e.g., but not limited to, as in Figs. 1A-5 above, for directly or indirectly using the LNG. The liquefied natural gas with the treated proppants is pumped as a cryogenic fluid at pressures and flow rates that are high enough, to fracture a subterranean formation SN. After fracturing operations are complete, the natural gas used as fracturing fluid can be recovered and re-used or commercialized. The LNG can be blended with proppants PT before or after pumping and is optionally heated either before it enters the well or during descent through the well bore.

"Liquefied natural gas" includes liquefied methane and blends of liquefied methane with any other normally gaseous hydrocarbons and/or atmospheric gases normally found in liquefied methane-based products and products generally referred to as "natural gas".

The fracturing system 15 includes a LNG source LS, for example a pressure vessel containing LNG can be any known LNG structure, unit, vessel, or source, e.g., a static structure, a mobile unit carried by a tanker truck, a train or a pipeline for on-site delivery of LNG to terrestrial wells, or by a tanker vessel for delivery to offshore wells. One or more cryogenic pump(s) CS associated with a fracturing rig pumps the LNG into the well WL equipped with wellhead isolation equipment WE mounted to a wellhead of the well. The wellhead isolation equipment includes surface fracture conduits SC ("frac lines"), chicksans, manifolds, and a wellhead or well tree isolation tool, all of which are well known. The well WL has a well bore extending through the subterranean formation SN.

The well system can include needed wellhead equipment, production tubing(s), hangers, casing, packers, risers, etc. Off-shore well systems can include sub-sea wellheads, as well as other components required for subsea wells. A cryogenically compatible delivery tubular DT conducts the LNG with the proppants PT down through a casing of the well. The tubular DT passes through any seals, packers or stuffing boxes (not shown) required to isolate the cryogenic fluid from a casing CG of the well. The liquefied natural gas with the proppants PT is pumped into the formation SN. Optionally, the proppants PT are blended with the liquefied natural gas using a blender BL prior to pumping the fracturing fluid into the well. Any suitable proppants may be used appropriately cryogenically treated according to the present invention. The cryogenic pumps CS pump the LNG/proppant mixture into the well WL. Optionally, the blending equipment may also be positioned upstream of the cryogenic pumps.

Optionally, the line conveying the LNG and proppants PT from the cryogenic pumps to the rig can be run through ocean water (or any other large body of water) to heat the LNG and to convert it to compressed natural gas (CNG) as the gas and the proppants are pumped to the wellhead isolation equipment. Optionally the proppants are cryogenically treated according to the present invention in association with or in LNG in any of the components of the system 15 (or with a separate dedicated system DS) rather than at or in the LNG Source itself (as indicated by the arrow AG).

In certain aspects, the present invention provides a fracturing fluid composition including: proppants cryogenically treated according to any method or process herein according to the present invention and a liquid component for temporarily supporting the proppants within the liquid component at surface, the liquid component including: i) a viscosified water component having a viscosity sufficient to temporarily support the proppants admixed within the viscosified water component; and optionally ii) a breaker for relaxing the viscosity of the viscosified water component within a pre-determined period. In certain aspects, the mass of proppant is 0.25-5.0 times the mass of the liquid component or 1.0-2.5 times the mass of the liquid component. For any method described herein in which proppants are cryogenically treated, any suitable other material to be treated may be treated by such a method, including, but not limited to any of the methods used with any system in any drawing figure.

In certain embodiments, the present invention provides methods of fracturing a formation within a well including the steps of: cryogenically treating proppants using any method or process according to the present invention disclosed herein and then preparing a liquid component at surface in a blender, the liquid component including a viscosified water component having a viscosity sufficient to temporarily support the proppants admixed within the viscosified water component; and, a breaker for relaxing the viscosity of the viscosified water component within a pre-determined period; mixing the proppant into the liquid component in the blender; introducing the proppant/liquid component into a high pressure pump and increasing the pressure to well pressure; optionally, introducing a gas component into the high pressure pump and increasing the pressure to well pressure; mixing the gas component, when present, with the proppant/liquid component; and, pumping the proppant/liquid mixture or the mixture combined the gas down the well.

As shown in Fig. 7, a well is fractured using a fluid that contains proppants that are cryogenically treated. Base fluids including water 10 (from water tank 10a), gelling agent 12, buffer 14, surfactant/alcohol 16 and breaker 18 (from a chemical truck 12a) are selectively introduced into a blender 20 (on blender truck 20a) at desired concentrations in accordance with the desired properties of the fluid composition.

Proppants 22 are cryogenically treated according to any method, system and process disclosed herein. Upon establishment of the desired viscosity of the fluid composition, proppants 22 (from proppant storage 22a) are added to the composition and blended prior to introduction into a high pressure pump 24 (on pump truck 24a). Optionally, gas 26 (from gas truck 26a) is introduced to a high pressure line between the high pressure pump 24 and a well 28 prior to introduction into the well 28. A data truck 30 is, optionally, configured to the equipment to collect and display real time data for controlling the equipment and to generate reports relating to the fracturing operation.

The blender blends the base fluids and proppants and chemical and includes appropriate inlets and valves for the introduction of the base fluids from the water tanks and chemical truck and proppant storage. The base liquid components including gum, buffer, surfactant, clay control, alcohol and breaker are delivered to a field site in a chemical truck 12a. The chemical truck includes all appropriate chemical totes, pumps, piping and computer control systems to deliver appropriate volumes of each base liquid component to the blender 20. Water tanks 10a include valves to deliver water to the blender via the blender hoses. Arrow AJ indicates that the proppants are cryogenically treated using cryogenic temperature supplied form any appropriate fluid and/or apparatus or item of the system shown in Fig. 7.

In certain aspects, with proppants cryogenically treated as described herein (according to any suitable system and method of the present invention), the present invention provides methods and systems of fracturing subterranean formations including: pumping metacritical phase natural gas or liquid natural gas into a subterranean formation to create or extend one or more fissures in the formation; and, optionally, maintaining or increasing pressure of the metacritical phase natural gas or liquid natural gas in the formation by pumping more metacritical phase natural gas and/or liquid natural gas into the fissures to hold the fissures open, and delivering the proppants into the subterranean formation with the gas to prop parts of the formation.

In certain aspects, with proppants cryogenically treated as described herein (according to any suitable system and method of the present invention), the present invention provides a fracturing process including: processing metacritical phase natural gas so it is at a temperature between about -150 degrees F and -220 degrees F and a pressure between about 700 and 800 psia; pumping the metacritical phase natural gas into a subterranean formation to create or extend one or more fissures in the formation; and delivering the proppants into the subterranean formation.

In certain aspects, with proppants cryogenically treated as described herein (according to any suitable system and method of the present invention), the present invention provides a fracturing system including: a metacritical phase natural gas supply processed so it is at a temperature between about -150 degrees F and -220 degrees F and a pressure between about 700 and 800 psia; and; a cryogenic storage tank for storing the metacritical phase natural gas at a temperature between about -150 degrees F and -220 degrees F and a pressure between about 700 and 800 psia, the cryogenic storage tank being fluidly connected to the metacritical phase natural gas supply; at least one positive displacement device fluidly connected to the cryogenic storage tank; a network of pipes fluidly connected to the at least one positive displacement device and the cryogenic storage tank, with at least one pipe extending into a subterranean formation; optionally, the metacritical phase natural gas supply can include an on-site natural gas plant configured to convert natural gas into metacritical phase natural gas by compression and refrigeration (which may be used for the cryogenic treatment of the present invention). The cryogenically treated proppants according to the present invention may utilize cryogenic fluid and/or cryogenic temperatures provided, directly or indirectly, from a component or components of this fracturing system (e.g., as in any of the systems of Figs. 1A - 6 above). In any of the meta-NG embodiments, the meta-NG may be pumped to a high pressure, warmed and used to deliver suitable proppants (cryogenically treated according to the present invention) to the fissures in the subterranean formations.

In certain embodiments, the present invention provides a method of fracturing subterranean formations, including pumping initial meta-NG into a subterranean formation to create or extend one or more fissures in the formation. The meta-NG may be produced on site. Methods may further include maintaining or increasing pressure of the initial meta-NG in the formation by pumping more - secondary - meta-NG into the fissures to hold the fissures open. In certain embodiments, cryogenically treated proppants according to the present invention are delivered into the subterranean formation by the meta-NG - initial, secondary, or both. Optionally the proppants may be lubricated and delivered via warm compressed natural gas ("CNG") at a high pressure.

Cryogenically treatment of proppants or of other material to be treated according to the present invention may utilize cryogenic fluid and/or cryogenic temperatures provided, directly or indirectly, from components of a fracturing system (hydraulic or non-hydrauic) which may include: an NG supply and/or a meta-NG supply, a cryogenic storage tank for storing the natural gas, at least one positive displacement device (e.g., a pump or compressor), and a network of pipes (which piping may include well casing and/or cement). The cryogenic storage tank is fluidly connected to the NG supply, and the positive displacement device is fluidly connected to the cryogenic storage tank. The network of pipes is fluidly connected to the at least one positive displacement device and the cryogenic storage tank, and at least one pipe extends into a subterranean formation. In exemplary embodiments, the NG is supplied by an on-site natural gas plant configured to convert natural gas into LNG and/or meta-NG by an appropriate balance of compression and refrigeration. Any component and the cryogenic fluid of any component may be used in the cryogenic treatment of the proppants, as indicated by the arrow AP, e.g., as in any of the systems and methods of Figs. 1A-6.

A system 20, shown in Fig. 8, has a sub-system 8 supplying meta-NG, a cryogenic storage tank 6 for storing the meta-NG, and a network of pipes 20a-20g connecting the above-ground equipment to the subterranean formation 18. The meta-NG supply equipment of the system 8 includes an array of production equipment, which may include different combinations of components such as a prime mover 22, which can be any suitable engine, a compressor 24, a chiller 26, a gas dryer 28, one or more meta-NG heat exchangers 30, and a cryogenic pump 32, and any other components, including but not limited to valves, sensors, and expanders, which together make up a natural gas plant 34 that can produce dense-phase meta-NG. It is within the scope of this invention to use any expander, turboexpander, expander valve, or part of an expander system, and/or part of a natural gas plant, e.g., but not limited to a turbine or associated apparatus and/or piping thereof, for supplying the cryogenic temperatures for cryogenically treating proppants according to any suitable embodiment of the present invention.

At least one positive displacement device is included in the equipment as well, i.e., the compressor 24 and the cryogenic pump 32 serve as the positive displacement device to move the meta-NG through the pipes into the subterranean formation 18.

The cryogenic storage tank 6 is fluidly connected via one or more pipes or other conduits to the meta-NG supply equipment 12 so the produced meta-NG can be stored for use. In turn, one or more of the positive displacement devices (i.e., the compressor 24 and the cryogenic pump 32) are fluidly connected to the cryogenic storage tank 6 and the meta-NG supply equipment 12. Finally, the network of pipes 20a-20f is in fluid connection with the positive displacement devices (i.e., the compressor 24 and the cryogenic pump 32) so they can effectively "pump" the meta-NG into the pipes. Although multiple configurations are possible, in an exemplary embodiment, positive displacement devices (compressor 24 and cryogenic pump 32) are connected to pipe 20b are at any other suitable desired location.

At least some of the underground piping may have perforations 21 in the horizontal pipes that allow the meta-NG 50a to enter the fissures 19 in the subterranean formation 18. The piping below ground, and within the hydrocarbon-bearing formation, is shown, where pipe 20c is the vertical piping that delivers the meta-NG 50a for fracking, and, in one embodiment, later a CNG-proppant stream 50c. Proppants may be in any of the liquid gas streams introduced into the formation. There is a return flow of warmed CNG 52, allowing for the rapid cool-down of the subterranean formation 18 that is being fractured.

Proppants may be delivered by a delivery system 42 which may act with a CNG system 36 for use in proppant delivery. CNG system 36 may include different combinations of components such as a CNG heat exchanger 38 to warm highly pressurized meta-NG 50a into high-pressure CNG 50b, as well as valves and program logic controls. Waste heat 23 can be the heat source for warming pumped-to-pressure meta-NG into CNG from the prime mover 22. A proppant hopper 40 is also provided, which is fluidly connected to the CNG system 36 to feed into line 42 into the high pressure CNG stream 50b exiting the CNG system 36.

In certain embodiments, the present invention provides systems and methods in which a tubing extending into a wellbore conveys liquid nitrogen (or some other liquid gas) from the earth surface to an earth formation. Such systems and methods (e.g., as in Figs. 1A-8, above) use cryogenic temperatures provided by the liquid nitrogen, either from the tubing itself, from surface equipment, and/or from mobile systems (e.g., trucking systems and tanks), to cryogenically treat proppants. One acceptable tubing material is a composite of fiber glass in a polymeric matrix, which maintains its strength at liquid nitrogen temperatures, and has a low heat conductivity.

The tubing may be adapted to connect to an above ground manifold, which can be of stainless steel, and stainless steel or other appropriate cryogenic piping can extend from the manifold to the liquid nitrogen source. In certain aspects, the liquid nitrogen source is one or more transportable tanks, each of which is connected to the manifold. Optionally, a gaseous nitrogen source also may be connected to the manifold by appropriate structure. The gaseous nitrogen source may be a liquid nitrogen tank with a heat exchanger at the tank's discharge for warming and gasifying nitrogen. Any of these items or structures - e.g., manifold, tubing, tank, piping heat exchanger - can be used to provide the cryogenic fluid and/or the cryogenic temperature for cryogenically treating proppants.

In certain aspects, with proppants cryogenically treated according to any suitable system and method of the present invention, the present invention provides methods for improving hydrocarbon fluid production from a cased wellbore extending into a subterranean formation including cryogenically treating proppants and: (a) providing a tubing in the wellbore for conveying liquid nitrogen from the surface to the formation, optionally the tubing having low thermal conductivity and comprised of composite fibers in a polymeric matrix; (b) providing a heat transfer barrier between the wellbore casing and the interior of the tubing; (c) injecting liquid nitrogen with the proppants through the tubing to the formation whereby the face of the wellbore adjacent the formation is contacted with liquid nitrogen and the proppants, and, optionally, during injection of the liquid nitrogen, flowing a gas down the annulus between the casing and the tubing; and (d) with the proppants propping the formation, producing hydrocarbon fluid from the formation through the wellbore.

In certain aspects, with proppants cryogenically treated according to any suitable system and method of the present invention, the present invention provides methods of improving hydrocarbon fluid production from a wellbore extending into a subterranean formation including cryogenically treating proppants and : (a) providing a wellbore from the surface through at least a portion of the formation; (b) casing the wellbore from the surface to adjacent the top of the formation; (c) providing a tubing string through the wellbore from the surface to a point adjacent the formation; (d) charging the formation by injecting the proppants and a gas down the wellbore and into the formation, optionally with the proppants in the gas; (e) optionally injecting a slug of water into said formation behind the injected gas;(f) and optionally injecting a gas behind the water slug to clear water from the tubing and wellbore; (g) injecting liquid nitrogen with the proppants into the formation at fracturing pressure; (h) displacing liquid nitrogen with the proppants into the formation from the tubing and borehole, the proppants propping parts of the formation; (i) closing the well to enable the liquid nitrogen to warm up and vaporize; and (j) opening the well to enable vaporized nitrogen to flow out followed by production of hydrocarbon fluid from the well.

In certain aspects, with proppants cryogenically treated according to any suitable system and method of the present invention, the present invention provides methods for increasing the permeability of a subterranean formation in the area of a wellbore penetrating the formation including cryogenically treating proppants and: injecting liquid gas, e.g., liquid helium or liquid nitrogen, through the tubing with the proppants treated according to the present invention to the formation to fracture parts of it and for the proppants to prop parts of it.

In certain aspects, the present invention provides a fracturing fluid including proppants (any proppant disclosed or referred to herein or part thereof) cryogenically treated according to any method or process herein according to the present invention, the fluid for hydraulically fracturing an underground formation penetrated by a well bore, the fluid including a liquified gas. In certain aspects, such a fluid is co-mingled with a non-liquified gas, wherein the liquified gas is liquified nitrogen, natural gas, or carbon dioxide and the non-liquified gas is one or more of nitrogen, air, exhaust gas, natural gas or inert gases, and wherein the fluid further includes the proppants, which, in one aspect, may be pressurized and cooled to substantially the pressure and temperature of the liquified gas prior to adding the proppants to the liquified gas. The proppants may be added to the liquified gas prior to co-mingling of the liquified gas with the non-liquified gas. Optionally, the concentration of the proppants may vary in the range from an amount in excess of 0 kg/m^3 to 1,550 kg/m^3. In one aspect, gaseous nitrogen is added to a stream of liquified carbon dioxide including proppants entrained therein.

In a system 90 according to the present invention, Fig. 9, proppants 980 are cryogenically treated according to any suitable method and system according to the present invention. As indicated by arrow AB, this treatment may utilize fluid at cryogenic temperature from any of the items of the system 90, Fig. 9. Liquified gas, e.g., liquified CO_2 (with or without proppants 980) is stored in a storage vessel or vessels 910 which may include transport vehicle(s) used to deliver the liquified gas to the site. The cryogenically-treated proppants 980 are stored in a pressure vessel 920. The proppants may be pressurized and cooled using some liquid CO2 from vessels 910 introduced into vessel 920 via a manifold or conduit and a tank pressure line. A blender 920 adds proppants 980 to liquid gas, e.g., liquid CO_2 volumetrically at a predetermined maximum rate. In one aspect, the previously-cryogenically-treated proppants 980 are cooled to a temperature of approximately -31 degrees C and subjected to a pressure of approximately 1,380 kPa. Optionally, and as is true for any method herein, proppants may be treated in or on the vessels 910; optionally on site or during transport to a site.

High pressure pumps 930 inject the fracture fluids into a well 950. Optionally, prior to the commencement of a fracturing process, the liquid CO_2 stored in vessels 10 is pressured up to a desired pressure above equilibrium pressure. The liquid $C0_2$ is pumped down into the well 950 which is a cased well, and then through perforations formed in the casing and into a formation FM. This liquefied gas may or may not contain proppants 980.

In one aspect, after sufficient liquified carbon dioxide has been injected into the well to create a fracture in the target formation, proppants 980 from the pressurized proppant tank 920 (which may include blending equipment) may be introduced into the streams of liquid carbon dioxide to be carried into the fracture by the carbon dioxide. The proppants may be any suitable known proppant, improved by cryogenic treatment according to the present invention -including any improvement in any parameter or measurement that is a factor is proppant performance and/or fracturing efficiency, including, but not limited to strength and sphericity; and may, in one aspect, include sand, e.g. silica sand, of any desired size, e.g., 40/60, 20/40 and 10/20 mesh size, coated or not, resin-coated or not. Other sizes and the use of other materials is contemplated depending upon the requirements of the job at hand.

Optionally, cooled proppants 980 may be introduced into the carbon dioxide stream simultaneously with the initial introduction of the liquified carbon dioxide into the formation for fracturing purposes. High pressure fracture pumpers 930 may be used for pumping a CO_2/proppant-980 mixture through a high pressure supply line 940 to the well 950 and down the well bore. The layout can additionally include a gas (e.g., nitrogen) booster 918 for vessels 910 and pressure vessel(s) 920. Nitrogen supply side can include storage vessels 960 for the gas, and high pressure gas pumpers 970 which pump the gas through supply line 965 to an intersection 945 with supply line 940. The intersection 945 in the supply line 940 is the point of initial contact between the streams of CO_2 and N_2 resulting in turbulence and forming a liquid CO_2/gas/proppant mixture, additional admixing occurring along the remaining length of supply line 940 and down the well.

It is within the scope of the present invention to cryogenically treat proppants (all or part thereof, or other material that may be treated) to achieve any of the goals stated in the text and including, but not limited to, to effect changes in the material of the proppants (or other material that may be treated) to enhance properties such as strength, shockability, hardness, wear resistance, toughness, durability, and dimensional stability; increased sphericity and reduced friction resistance; surface smoothness, to reduce fines production; to inhibit anchoring of undesirable material to a proppant surface or surface of other material to be treated; to provide cracks and/or microcracks in all or part of a proppant (or other material that may be treated), e.g., in a proppant (or other material that may be treated) core, in proppant (or other material that may be treated) layer(s), and/or in proppant (or other material that may be treated) coating(s), the cracks and/or microcracks for stress relief and/or for enhancing dimensional stability and/or to provide fluid pathway(s) to reduce proppant blockage of fluid and/or hydrocarbons to be produced and to facilitate such production. To achieve these and any of the other goals of cryogenic treatment of proppants (or other material that may be treated), any suitable cryogenic treatment method, regime, program, cycle, cycles, and protocol may be employed. The method, etc.

chosen, in certain aspects, may be affected by the proppant material (or other material that may be treated), density, weight, and other properties of the proppant (or other material that may be treated), as well as by the goal to be achieved. For example, many methods and processes are known for treating a variety of materials cryogenically and a variety of materials are used for proppants (e.g., core and/or coating can include, inter alia, sand, ceramics, glass, sintered bauxite, bauxite, composites, metals, polymers, walnut hulls, and plastics). Such methods may be used, inter alia, according to the present invention to cryogenically treat proppants (or other material that may be treated). In one method, proppants (or other material that may be treated) are cooled over 36 to 74 hours from room temperature to 77 degrees K, held there for 20 to 30 hours, and then ramped up back to room temperature over 10 to 20 hours. Proppants (or other material that may be treated) may be cooled at any suitable desired cooling rate, e.g., but not limited to, between 0.3°K/minute to 1.2°K/minute or 0.5° C/minute. In one method, proppants (or other material that may be treated), e.g., but not limited to, sand and ceramics, are cryo treated at a treating temperature of about -304 degrees C. for a residence time of about 24 hours, ramped down to the treating temperature over a period of about 6-8 hours, and ramped up back to ambient for a period of about 6-8 hours. In one method, proppants are ramped down to 80K (-193 degrees C) over a 6 to 8 hour period; held at -193 degrees C for 8 to 24 hours; and then ramped up to ambient temperature in a time period of 8 to 24 hours.

In certain aspects, proppants (or other material that may be treated) may be cryogenically treated according to the present invention with a shallow cryogenic treatment (SCT) or a deep cryogenic treatment (DCT). There are known SCTs and DCTs for a variety of materials that may be used for proppants (or other material that may be treated) of these materials. In certain aspects, proppants (or other material that may be treated) may be treated with an SCT which includes: placing proppants (or other material that may be treated) in a freezer at 193 degrees K and then bringing them back to room temperature; cooling the proppants (or other material that may be treated) to between -60 degrees C and -80 degrees C; cooling the proppants (or other material that may be treated) to -60 degrees C and holding them there for 5 hours; cool the proppants (or other material that may be treated) to -110 degrees C and holding them there for 18 to 25 hours, then a 4 hour ramp up to room temperature. Any SCT can include any suitable warming ramp-up cycle and/or tempering cycle. In certain aspects, proppants (or other material that may be treated) may be treated by a DCT that includes: slowly cool proppants (or other material that may be treated) to 77 degrees K, hold at this temperature for several or many hours, and gradually warm the proppants (or other material that may be treated) to room temperature; cool proppants (or other material that may be treated) to -196 degrees C and hold there for 24 hours; cool proppants to -196 degrees C (-320 degrees F), hold there for between 24 to 72 hours, and then ramp up to room temperature over 7 hours.

It is within the scope of the present invention, in certain embodiments, to treat proppants (depending on the material and the material properties, e.g., shape, density, weight) (or other material that may be treated) with the methods and using the equipment as disclosed in the following U.S. Patents and U.S. Patent applications, with suitable modifications and/or programming if needed according the present invention, to effect a cryogenic treatment according to the present invention (and in the references cited in these), all incorporated fully herein for all purposes: U.S. Patents 5,188,175; 3,929,191; 5,865,913; 4,667,478; 3,881,322; 5,715,688; 5,447,035; 6,109,064; 6,588,218; 6,026,648;8,235,767; 8,496,057; 6,332,325; 5,970,717; 5,701,745; 5,309,722; 5,259,200; 4,484,988; 6,544,669; 4,253,314; 4,237,695; 4,072,026; and U.S. Applications Serial Numbers 10/753,933 20 Feb. 2004; 11/582,644 published 15 Feb. 2007; 12/072,337 25 Feb. 2008; 12/925,165 14 Oct. 2010; 12/343,130 23 Dec. 2008; 13/548,243 filed 13 July 201; 13/044,692 filed 10 March 2011; 11/283,381 filed 18 Nov. 2005; and 10/246,568 18 Sep. 2002. With respect to these proppants (or other material that may be treated), and to any proppants (or other material that may be treated), according to the present invention for proppants which are not all one material, any component material of a proppant (or other material that may be treated) may be treated cryogenically, using any suitable method disclosed herein, before a final proppant is made with such material. Also, for a multi-component proppant, at any stage of the making of such a proppant, the intermediate stage may be cryogenically treated according to the present invention. For example, a proppant to be coated may be treated before coating; or a proppant with multiple distinct coatings or layers may be cryogenically treated after the application of a first layer or after the application of any subsequent layer.

It is within the scope of the present invention to continuously treat proppants (or other material that may be treated) cryogenically with a system that includes movement apparatus for moving proppants (or other material that may be treated) adjacent, through, under or over a cryogenic fluid or a member at cryogenic temperature, by direct or indirect encounter of the cryogenic fluid. In one aspect, proppants on a movement apparatus, e.g., an endless belt, auger system, or a rotating support, are treated at cryogenic temperature by cryogenic fluid injected onto, immersing, or sprayed onto the proppants or by the belt or support being maintained at cryogenic temperature.

With appropriate modifications and/or programming according to the present invention to effect a proppant cryogenic treatment according to the present invention, the systems and methods of these U.S. Patents, and those in references cited in these patents, may be used for the treatment and/or continuous treatment of proppants or other material that may be treated) (all said patents incorporated fully herein for all purposes): U.S. Patents 4,075,869; 4,195,490; 4,276,753; 4,644,754; 4,852,358; 4,989,416; 5,460,015; 5,467,612; 5,520,004; and 6,070,416; and U.S. Patent Applications Pub. No. 2012/0255315.

In certain aspects, e.g., as shown in Fig. 10, the present invention provides a proppant which has a core CO and a coating CT. In certain aspects, the core is a particle made of any suitable known material for a proppant, e.g., but no limited to, sand, pebbles, gravel, glass, ceramic, composite, silica, natural particle material, metal particle, synthetic organic particle and sintered bauxite; and the coating may be any suitable known resin-coating, with or without nanomaterial therein, with or without carbon nanotubes therein. The core may be a a non-deformable core with its entire surface surrounded by at least one coating or layer. According to the present invention, the core is cryogenically treated either before or after coating (e.g., using any system and method herein according to the present invention). According to the present invention, a component or components of a coating (or other material that may be treated) may be cryogenically treated according to the present invention before the coating is applied to a core or to a layer already present, or the coating can be cryogenically treated after it is applied to the core.

In certain aspects, e.g., as shown in Fig. 11, a resin-coated particle PT, which may be a non-deformable particulate core, is surrounded by a series of interlocking, integrated coatings or layers CL. Optionally the coating or layers are one within the other; or each layer of coating is interleaved with the others. The core of the proppant of Fig. 10 and the core and layers of the proppant of Fig. 11 may be as disclosed in U.S. Patent 7,135,231.

Resins useful for the proppants of Figs. 10 and 11 may include novolac resins, epoxy resins, resole resins, phenol-aldehyde resins, urea-aldehyde resins, furfuryl alcohol resins, melamine resins, polyester resins, and alkyl resins. Any of the proppants of Figs. 10 and 11 may have a reinforcing agent in the core, in a layer or layers, or both; e.g., a reinforcing agent which is metal, carbide, plastic, ceramic, composite and which may be a nanoparticle of natural clays, synthetic clays, layered clays, inorganic metal oxides, impact modifiers, and mixtures thereof. Any such agent may be cryogenically teated before or after incorporation into a coating or layer.

It is within the scope of the present invention to treat (with any suitable method or methods according to the present invention) proppants (or other material that may be treated), proppants with or without a coating, solid or hollow and/or with an internal filler or core material, (treating a core, treating a coating or layer, or both), such proppants as disclosed in the following U.S. Patents (before treatment according to the present invention) and in the references cited in these patents all of which, patents and references, are incorporated fully herein by reference: U.S. Patents 4,068,718; 3,492,147; 3,929,191; 5,643,669; 5,916,933; 6,059,034; 6,328,105; 6,406,789; 8,298,667; 8,273,406; 8,236,737; 8,216,675; 8,193,128; 8,186,434; 8,178,436; 8,075,997; 8,063,000; 8,012,533; 8,003,212; 7,950,455; 7,931,087; 7,914,892; 7,887,918; 7,883,773; 7,867,613; 7,828,998; 7,825,053; 7,721,804; 7,678,723; 7,615,172; 7,560,690; 7,491,444; 7,459,209; 7,135,231; 8,006,759; 8,119,576; and 8,596,361.

It is within the scope of the present invention to thermally treat a proppant (or other material that may be treated) to provide permanent cracks and/or microcracks in all or part of the proppant body (or other material that may be treated). In one aspect, such cracks and/or microcracks, provide stress relief when the proppant is stressed, e.g., when it is in place propping part of a formation. In one aspect, the thermal treatment is cryogenic treating with a cooling step or steps (or "ramp down"), optionally a resident time at low temperature, and then a heat-up step or steps ("ramp up") in which the proppant is returned to ambient temperature. In one aspect, a previously-known cryogenic treatment method is used which in the past was done so as to reduce or eliminate microcracking, but, according to the present invention, is now used to provide desired microcracking and modified so that microcracking is controlled, located in a desired part or all of a proppant body, and not eliminated from the proppant body. In particular aspects, only a core or central part of a proppant body has microcracks. In particular aspects, only a surface or area near a proppant surface has microcracks. In certain aspects, both a core and a coating or layer, or coatings or layers, of a proppant have microcracks.

As shown in Fig. 12A, a proppant Px has a body made of any suitable known material which has been cryogenically treated using any system and method according to the present invention so that, upon completion of the method, the finished proppant has therein microcracks Mx. The method is conducted so that the microcracks form and so that they are not eliminated either by the cooling step(s) or by the heating step(s).

As shown in Fig. 12B, a proppant Py has a body with a core Ry made of any suitable known material and a coating Cy made of any suitable known coating material for proppants and the proppant Py has been cryogenically treated using any system and method according to the present invention so that, upon completion of the method, the finished proppant has therein microcracks My in the core and microcracks Mb in the coating. The method is conducted so that the microcracks form and so that they are not eliminated either by the cooling step(s) or by the heating step(s). The microcracks in the core or in the coating may be deleted.

As shown in Fig. 12C, a proppant Pz has a body made of any suitable known material which has been cryogenically treated using any system and method according to the present invention so that, upon completion of the method, the finished proppant has an outer volume Cz with microcracks Mz. The method is conducted so that the microcracks form and so that they are not eliminated either by the cooling step(s) or by the heating step(s).

As shown in Fig. 12D, a proppant Ps has a body made of any suitable known material which has been cryogenically treated using any system and method according to the present invention so that, upon completion of the method, the finished proppant has a central volume Cs with microcracks Ms. The method is conducted so that the microcracks form and so that they are not eliminated either by the cooling step(s) or by the heating step(s).

As shown in Fig. 13A, a proppant Pv has a body made of any suitable known material which has been cryogenically treated using any system and method according to the present invention so that, upon completion of the method, the finished proppant has microcracks Mv which are in fluid communication with each other such that a fluid flow path is provided through the proppant.

As shown in Fig. 13B, a proppant Pt has a core Rt made of any suitable known material which has been cryogenically treated using any system and method according to the present invention and a coating Gt which is treated according to any suitable system and method of the present invention, so that, upon completion of the treatment of the core and coating, the finished proppant has microcracks Mt and Mu which are in fluid communication with each other such that a fluid flow path is provided through the proppant.

Fig. 14A shows a proppant Pp according to the present invention with particles of reinforcement Fp; which may be, for example, pieces or particles of rubber, elastomer, polymers, plastic, nanoclay, or carboxyl-functionalized rubber; or nanomaterial, e.g., but not limited to nanotubes, e.g., but not limited to carbon nanotubes. Optionally, any reinforcement agent disclosed or referred to herein or in references incorporated herein may be used. The proppant Pp is cryogenically treated so that desired microcracks (e.g. as in Figs. 12A-13B) are created with the reinforcement Fp influencing the number, extent, dimensions, and location of the microcracks. Fig. 14B shows a proppant Pn according to the present invention with a core En with particles of reinforcement Fn and a coating Gn with particles of reinforcement Nn; which particles, Fn and Nn may be, for example, pieces or particles of rubber, elastomer, polymers, plastic, nanoclay, nanomaterial, or carboxyl-functionalized rubber. Optionally, any reinforcement agent disclosed or referred to herein or in references incorporated herein may be used. The proppant Pn is and the coating Gn are cryogenically treated according to any suitable system and method

Figs. 13A and 13B, the reinforcements discussed in the preceding two paragraphs (and, e.g., as shown in Figs. 14A and 14B) may be employed and so located that fluid flow paths are formed in desired number(s), in desired parts, and/or in desired areas of a proppant. of the present invention so that desired microcracks (e.g. as in Figs. 12A-13B) are created with the reinforcement Fp influencing the number, extent, dimensions, and location of the microcracks. Any reinforcements herein may be used in any proppant, with or without microcracking.

With respect to proppants as in Figs. 13A and 13B, the reinforcements discussed in preceding paragraphs (and e.g., as shown in Figs. 14A and 14B) may be employed and so located that flow paths are formed in desired number(s), in desired parts, and/or in desired areas of a proppant.

It is within the scope of the present invention, by cryogenically treating proppants (or other material that may be treated), to improve shape (e.g. sphericity), to smooth a proppant's (or other material that may be treated) surface, to reduce friction between proppants (or pieces or particles of other material that may be treated), to reduce prominent projections as compared to untreated proppants (or other material that may be treated); to inhibit anchoring of undesirable materials to a surface; and/or to reduce produced fines. In addition it is within the scope of the present invention to subject cryogenically treated proppants (or other material to be treated) to additional shaping so that smoothness and/or sphericity is/are further increased and/or so that treated proppants (or pieces or particles of other material that may be treated) flow more easily with less friction.

Cryogenically treated proppants (or other material that may be treated) according to the present invention, in certain aspects, are further processed by a shaping structure that may be any known apparatus, device, equipment, conduit, or machine that further increases the proppants' sphericity, smooths proppant surfaces, reduces projections from proppants, and/or reduces frictional resistance to proppant flow. Such apparatus includes, but is not limited to, mills, abrasive-attritioning systems, screen(s), screening systems, pulverizers, blast tube systems, pneumatic target systems, grinders, tumblers, shakers, and hammermills - and includes systems as in U.S. Patent Publications 2011/0290917 and 2013/0167562. In a particular aspect, the shaper may be a flow conduit through which the proppants flow (up, down, horizontally, or at an incline) which has therein one or more members which the proppants strike, thereby further enhancing sphericity, etc.; and such flow may be in any suitable fluid, e.g., liquid or pressurized gas or a pneumatic fluid flow that conveys the proppants.

Fig. 15 shows schematically a system 200 in which proppants Pa (or other material that may be treated) are fed to a cryogenic treatment system 201 for cryogenic treatement according to any aspect or embodiment of the present invention. Cryogenically treated proppants Pb which have been enhanced by the cryogenic treatement according to the present invention are then fed to a shaper 202 for further shape enhancement, e.g., to smooth surfaces and/or increase sphericity. Final shape proppants Pc exit the shaper 202. The shaper 202 may be any structure or apparatus, etc. which further enhances proppant shape.

Sand useful as proppants as shown in Figs. 16A and 16B has the shapes shown in those figures prior to any cryogenic treating according to the present invention. Scanning electron microscope pictures of the sand - Figs. 17A - 17B - indicates the condition of the surface of the sand particles prior to any treatment.

The sand was treated cryogenically in a chamber in which the temperature was ramped down over a period of about eight hours from ambient to -304 degrees C. The sand was then maintained at this temperature for about 24 hours. The temperature was then ramped up to ambient over a period of about eight hours. Ceramic bead proppants were also treated by such a method.

As shown in Figs. 18A - 18C sphericity of the sand has been enhanced, the surfaces of the sand particles have been smoothed, and there are less prominent projections from the sand particles as compared to the untreated sand. Figs. 19A and 19B provide scanning electron microscope pictures of the cryogenically-treated for comparison with the surfaces in Figs. 17A - 17B.

The specific cryogenic treatment used for the sand of Fig. 16A may also be used for particular embodiments of treating ceramic bead or glass bead proppants (or other material that may be treated) according to the present invention.

Ceramic beads useful as proppants as shown in Fig. 20A have the shapes shown in this figure prior to any cryogenic treating according to the present invention. Scanning electron microscope pictures of the untreated proppants - Figs. 20b and 20C - indicate the condition of the surface of the ceramic beads prior to any treatment.

The proppants were treated cryogenically in a chamber in which the temperature was ramped down over a period of about eight hours from ambient to -304 degrees C. The proppants were then maintained at this temperature for about 24 hours. The temperature was then ramped up to ambient over a period of about eight hours. As with the sand, any suitable ramp down and ramp up times may be used.

As shown in Figs. 21A there is some, but minimal, enhancement of sphericity of the ceramic bead proppants; and, the surfaces of the ceramic bead proppants have been smoothed (see Figs. 21B and 21C), and there are less prominent projections as compared to the untreated beads.

Undesirable fine particles - "fines" - can be produced by inter-proppant contacts and impacts (or such contact of pieces or particles of other material that may be treated), by contacts and impacts of proppants with other materials, and by contacts and impacts with things such as parts of equipment through which proppants flow, interior surfaces of conduits and piping, and interiors of pumps and valves. Enhancing proppants (or other material that may be treated) according to the present invention - e.g. making more spherical proppants (or other material that may be treated), smoothing proppant (or other material that may be treated)surfaces, and/or reducing projections from proppant bodies - can result in the production of relatively less fines due to such contacts and impacts. Fines production may also be produced by providing a relatively stronger proppant (or other material that may be treated).

It is within the scope of the present invention to cryogenically treat nanomaterial used with proppants. It is within the scope of the present invention to cryogenically treat nanomaterial used or to be used in or on a proppant or any part of a proppant; e.g, but not limited to, within a solid proppant, on a solid proppant, within a hollow proppant, in a coating of a proppant, or in any layer or part of a multi-layer or multi-part proppant. It is within the scope of the present invention to cryogenically treat nanomaterial including, but not limited to used in or on a proppant, whether the nanomaterial is dispersed, agglomerated, or in discrete masses or amounts. Any suitable treatment disclosed or referred to herein may be used for the treatment of nanomaterial; including, but not limited to, the cryogenic treatment of nanotubes, including the cryonenic treatment of carbon nanotubes.

It is within the scope of the present invention to cryogenically treat nanomaterial whether used in or on a proppant or not. It is within the scope of the present invention to cryogenically treat nanomaterial used or to be used in or on a composite, a coating, a film,, a paste, a laminate, a web, a mesh, a fabric,a piece of plastic, or a polymer. It is within the scope of the present invention to cryogenically treat nanomaterial including nanomaterial dispersed, agglomerated, or in discrete masses or amounts. Any suitable treatment disclosed or referred to herein may be used for the treatment of nanomaterial; including, but not limited to, the cryogenic treatment of nanotubes, including the cryogenic treatment of carbon nanotubes.

The present invention includes cryogenically treated nanomaterial. The nanomaterial may be, inter alia, but not limited to e.g., molecules and structures with at least one dimension roughly between 1 and 100 nanometers or between 1 and 500 nm. "Nanomaterial" may include nanoparticles, nanotubes, nanostructures, nanocomposites, nanopastes, nanohorns, coated *nanomaterial,* nanomatrices, ceramic nanomatrices, nanoplatlets, nanoflakes, nanoribbons, nanographene, transformed nanomaterial, nanowires, nanorods, nanopillars, nanofibrils, nanospheres, nanobelt, nanosheet, nanocard, nanoprism, quantum dot, quantum wires, carbon nanotubes, single-wall carbon nanotubes (SWNTs), multi-wall carbon nanotubes (MWNTs), double-wall carbon nanotubes (DWNTs), buckytubes, fullerene tubes, tubular fullerenes, graphite fibrils, carbon nanofibers, functionalized nanotubes, graphene, and combinations of two or more of these.

According to the present invention, nanomaterial ("NM") may be treated by any suitable cryogenic treatment described herein wherein the NM is treated by taking the nanomaterial down to a selected cryogenic temperature, maintaining the nanomaterial for a selected time at the cryogenic temperature, and then bringing the nanomaterial back up to a selected temperature, e.g., to ambient temperature, over a selected time period.

In certain aspects, the NM is treated with a shallow cryogenic treatment ("SCT"). In certain aspects the SCT is an SCT which is one of: subjecting NM to a temperature of 193 degrees K and then bringing the NM back to room temperature; cooling the NM to between -60 degrees C and -80 degrees C; cooling the NM to -60 degrees C and holding the NM there for about 5 hours; or cooling the NM -110 degrees C and holding the NM there for 18 to 25 hours, and then over about 4 hours ramping up the NM to room temperature. Any of these SCTs may be used to treat carbon nanotubes, inter alia.

In certain aspects, the NM is treated with a deep cryogenic treatment (DCT"). In certain aspects, the DCT is a DCT which is one of: slowly cooling NM to 77 degrees K, holding the NM at 77 degrees K for any selected time period of hours, and then gradually warming the NM to room temperature; cooling NM to -196 degrees C and holding the NM at said temperature for about 24 hours; cooling NM to -196 degrees C (-320 degrees F), holding the NM at said temperature for between 24 to 72 hours, and then warming the N by ramping up to room temperature over a period of about 7 hours. Any of these DCTs may be used to treat carbon nanotubes, inter alia.

In certain aspects, NM is treated by cooling the NM over 36 to 74 hours from room temperature to about 77 degrees K, holding the NM at this temperature for 20 to 30 hours, and then warming the NM by ramping up back to room temperature over 10 to 20 hours.

In certain aspects, for any treatment method, NM is treated by cooling the NM at a cooling rate between 0.3°K/minute to 1.2°K/minute or 0.5° C/minute.

In certain aspects, NM is treated at a treating temperature, in one aspect a treating temperature of about -304 degrees C, for a residence time of about 24 hours, wherein the NM is ramped down to the treating temperature over a period of about 6-8 hours, and the temperature is then ramped up back to ambient over a period of about 6-8 hours.

In certain aspects, NM is treated at a treating temperature of about 80K (-193 degrees C), being ramped down to treating temperature over a 6 to 8 hour period; held at about -193 degrees C for 8 to 24 hours; and then heating the NM by ramping up the temperature to ambient temperature in a time period of 8 to 24 hours. As in the other NM treatment descriptions herein, the NM may be carbon nanotubes.

In certain aspects, NM is cryogenically treated by thermally cycling the NM at temperatures between -100 degrees F. and -300 degrees F. and including a final thermal treatment step or steps of heating, e.g., but not limityed to, heating the NM from a cryogenic temperature or form an ambient temperature up to an elevated temperature, e.g. between about +200 degrees F. and +300 degrees. F. and then cooling the NM to ambient temperature.

Any NM treatment herein may be used to treat NM alone, separate pieces or particles of NM, or NM with, in, or on other material, mesh, composite, fabric, web or cloth. When NM is with, in or on other material the cryogenic treatment chosen may be altered or adjusted depending on the nature, location, and amount of the other material. Cryogenic treatment of NM alone or NM with, in or on other material, etc. may be done at any suitable point in the use of the NM and/or in the use and/or making or fabrication of the NM alone or the NM with the other material. In certain aspects, the other material alone is treated or the NM alone is treated. Such a cryogenic treatment may be done at any point in a process or method for using or incorporating NM or at any step in a making or fabrication process or method for making or fabricating an item. A finished item with NM therein and/or thereon may be cryogenically treated according to the present invention. As is true for any NM herein, any proppant herein, any such NM, etc. may be subjected to multiple cryogenic treatments, either similar or different.

Nanomaterials (including, but not limited to, carbon nanotubes) are cryogenically treated in accord with any suitable cryogenic treatment herein to: increase strength, improve shape characteristics, to reduce prominent parts or projections as compared to untreated material, reduce friction, smooth surfaces, reduce fines production, improve thermal properties, improve electrical properties, reduce electrical resistance, improve electrical conductivity of conductive nanomaterials, reduce anchoring of undesirable materials to the surfaces of treated materials, and/or improved surface characteristics which enhance various uses.

The present invention provides, in certain aspects, the cryogenic treatment of a composite that has a matrix and aggregated amounts, masses, agglomerations, and spaced-apart discrete units with multiple pieces, tubes or particles of nanomaterial (e.g., but not limited to, carbon nanotubes) - all collectively referred to as "units." The present invention provides cryogenic treatment of a finished composite with matrix material and nanomaterial units; but also, in certain aspects, the cryogenic treatment of the units before they are introduced into the matrix and/or the cryogenic treatment of the matrix before the nanomaterial units are introduced therein. It is also within the scope of the present invention to cryogenically treat the pieces, etc. of nanomaterial before the pieces, etc. are aggregated or assembled into a unit. Without limitation, the matrix may be a polymer; without limitation, any material used for a proppant or on or in a proppant; without limitation, a thermoelectric matrix including a thermoelectric material; and without limitation, the nanomaterial may be in units spaced apart from each other, e.g., but not limited to, with a spacing between two neighboring nanotubes of about 50 nm to 2 micrometers. A unit may contain any desired amount, weight, proportion, or number of pieces of nanomaterial; in certain aspects, this is an amount sufficient to effect any of the results and/or goals of cryogenic treatment.

Optionally, the units and/or the matrix may be as disclosed in U.S. Application Pub. No. 2013/0153819, incorporated fully herein for all purposes. Optionally, the matrix is any matrix disclosed herein or referred to herein, or is any material disclosed herein which contains or can contain units of nanomaterial - all collectively referred to as "matrix material."

Fig. 22 shows a composite 220 according to the present invention which has a matrix 2210 of matrix material and a plurality of nanomaterial units 2220. Optionally the matrix is a polymer; optionally the matrix is any material used for any composite containing nanomaterial; and/or optionally the matrix is thermoelectric matrix material.

The units 2220 may be spaced-apart by any desired distance and they may be of any desired volume, shape and size. In certain aspects, the spacing between two neighboring units may be about 50 nm to 2 µm, about 200 nm to 1 µm, about 400 nm to 700 nm, or about 400 nm to 500 nm. The term "spacing" here means a spacing between two neighboring units 120 in any direction. The units need not be all spaced-apart the same distance.

Optionally, the matrix 2210 is be formed on a substrate 2230. Optionally the substrate is electrically insulated from the matrix.

In certain aspects, the present invention provides a composite material, including: a matrix of matrix material; and a plurality of nanomaterial units located in the matrix and spaced apart from each other, wherein optionally a pacing between two neighboring units is about 50 nm to 2 µm. The units may be in any desired shape, including, but not limited to an undefined mass, random, or amorphous shape. In certain aspects, the shape of the units is spherical, cylindrical, particulate, cubic, or columnar. The units may be present in the matrix in any pattern or order, in any layer or layers, at or near any surface or surfaces, including a columnar shape embedded in the matrix along a single direction or along different directions. The units, optionally, are arranged in a one-dimensional array, a two-dimensional array, or in a random manner in the matrix. Any units may be arranged in equal intervals or at different intervals.

It is within the scope of the present invention to provide a composite which includes matrix material within which is nanomaterial, e.g., but not limited to, a composite that is an armor structure, an antiballistic composite, or a laminate in which the finished product is cryogenically treated and/or components before incorporation into the matrix are cryogenically treated. In one aspect, the present invention provides a composite 2330 as shown in Fig. 23 which has an optional substrate 2339. Such a composite may be a structural unit for incorporation with a thin, item or host. A composite matrix 2332 includes a multiplicity of pieces, parts, masses, or particulate units 2336, e.g., but not limited to, polymeric molecules or material, metallic molecules or ceramic molecules, The composite matrix 2332 includes a multiplicity of interstices 2337 formed at the juncture of a plurality of particulate units 2336. In the multiplicity of interstices 137 are a multiplicity of pieces, parts, or molecules of nanomaterial 133, e.g., carbon nanotubes. In certain aspects in anantiballistic composite 2330, an array is defined by a multiplicity of single-walled carbon nanotubes disbursed within the interstices 2337.

The matrix material 2332 may be any matrix material disclosed or referred to herein. The matrix material may be any matrix material and the nanomaterial may be any nanomaterial referred to in U.S. Patent Application Pub. No. 2005/0158551. Optionally the matrix material is a ceramic material as disclosed in U.S. Patent 6,858,173.

It is within the present invention to cryogenically treat fabric, cloth, networks, arrays, textiles, mesh, woven material, nonwoven material, tile, web, or felt material that is made of, or which contains, nanomaterial. Figs. 24A, 23B, and 24C depict individual layers of a fabric according to the present invention where the mechanical, electrical, thermal, surface, strength, and/or chemical properties of the fabric are improved by cryogenically treating the finished fabric and/or by cryogenically treating the component(s) of the fabric prior to or during addition to or manufacture of the fabric.

Fig 24A depicts a layer of woven fabric 2440 wherein fibers 2442 are woven to form a matrix. Nanomaterial 2442, e.g. any nanomaterial disclosed or referred to herein, e.g. nanotubes, e.g. carbon nanotubes, are made, added to, synthesized or grown within interstices 2443 between and/or on fibers 2442. The nanomaterial, e.g. nanotubes, may be anchored to individual fibers 2442 and become entangled with other nanomaterial and fibers. This entanglement can allow the fabric to disperse or absorb force and displace pressure of an impacting object. In certain aspects, the fibers distribute loads globally while the nanomaterial distributes loads locally (nonsocial) to achieve a tiered mechanism with which to distribute mechanical loads.

Fig. 24B depicts a layer of fabric 2444 wherein fibers 2445 are laid or felted together to form the layer. As seen in the woven fabric of Fig. 24A, nanomaterial 2446, e.g. but not limited to nanotubes, is made, grown, added to, or synthesized within interstices 2443 located between felted fibers 2445. A laid fabric, web, or felt may be made by air laying and a felted fabric may be made by fiber deposition, e.g. by vacuum deposition of fibers.

Fig. 24C depicts a layer of knitted fabric 2448 with fibers 2449 knitted to form fabric. This can allow a greater mechanical coupling of the fibers within the fabric to further improve the mechanical coupling of the fibers. Nanotubes 2447 are made, added to, grown, or synthesized within interstices 2443 and may be anchored to fibers 2449, e.g but not limited to, with catalyst particles.

It is within the scope of the present invention to cryogenically treat nanotubes and arrays, networks or mesh, e.g., but not limited to, as disclosed in U.S. Patent Applications Pub. Nos. 2009/0110897 and 2003/0044608 and U.S. Patent 6,781,166.

Any nanomaterial herein in any shape or form initially, before, or after treatment, may be formed into a shape for use as a proppant or a part of component of a proppant; including, but not limited to, any nanomaterial disclosed herein as, or as a part of component of, a composite, matrix, web, mesh, fabric, laminate, or paste; and such a composite etc. itself with nanomaterial therein may be formed into a shape as a proppant or as part of a proppant, including, but not limited to, the fabrics, composites, mesh, webs, pastes, laminates, and matrices disclosed herein.

It is within the scope of the present invention to cryogenically treat, with any suitable cryogenic treatment, electrically conductive nanomaterial to enhance its electrical properties, inter alia, its electrical conductivity. In certain aspects, this conductive nanomaterial is electrically conductive nanotubes; e.g., but not limited to, carbon nanomaterial, e.g., but not limited to, carbon nanotubes. In certain aspects, electrically conductive nanotubes functionalized with an electrically conductive material, e.g., but not limited to, silver, aluminum, copper, or carbon, are cryogenically treated using any suitable cryogenic treatment disclosed or referred to herein; including, but not limited to, any suitable SCT or DCT. In one aspect, the treatment includes: subjecting the carbon nanotubes to a cryogenic treatment temperature by ramping the temperature of the nanotubes down over a period of about 8 hours from ambient to a treatment temperature of about -304 degrees C; maintaining this treatment temperature for about 24 hours; and then ramping the temperature up to ambient over a period of about 8 hours.

All patents and patent applications cited herein are incorporated fully herein for all purposes. This invention is susceptible to various modifications and alternatives, and described embodiments are not intended to limit the invention to the particular forms disclosed.

With regard to claims whether now or later presented for examination, it should be understood that for practical reasons and so as to avoid great expansion of the examination burden, the inventors may at any time present only initial claims or perhaps only initial claims with only initial dependencies. Support should be understood to exist to the degree required under new matter laws - including but not limited to European Patent Convention Article 123(2) and United States Patent Law 35 USC 132 or other such laws - to permit the addition of any of the various dependencies or other elements presented under one independent claim or concept as dependencies or elements under any other independent claim or concept. In drafting any claims at any time whether in this application or in any subsequent application, it should also be understood that the applicant has intended to capture as full and broad a scope of coverage as legally available.

Any claims set forth at any time during the pendency of the application for this patent or offspring of it are hereby incorporated by reference as part of this description of the invention, and the applicant expressly reserves the right to use all of or a portion of such incorporated content of such claims as additional description to support any of or all of the claims or any element or component thereof, and the applicant further expressly reserves the right to move any portion of or all of the incorporated content of such claims or any element or component thereof from the description into the claims or vice-versa as necessary to define the matter for which protection is sought by this application or by any subsequent continuation, division, or continuation-in-part application thereof, or to obtain any benefit of, reduction in fees pursuant to, or to comply with the patent laws, rules, or regulations of any country or treaty, and such content incorporated by reference shall survive during the entire pendency of this application including any subsequent continuation, division, or continuation-in-part application thereof or any reissue or extension thereon.

What is claimed is:

1. A cryogenically treated proppant.

2. The proppant of claim 1 cryogencially treated with a treatment comprising:
   introducing the proppant into a chamber;
   ramping the temperature down over a period of about eight hours from ambient to a treatment temperature of about -304 degrees C;
   maintaining this treatment temperature for about 24 hours; and then
   ramping the temperature up to ambient over a period of about eight hours.
3. The proppant of claim 2 wherein the proppant is sand or ceramic.

4. The proppant of claim 1 cryogenically treated with a treatment which is one of a SCT; a DCT; and introducing the proppant into a chamber, ramping the temperature down over a period of about eight hours from ambient to a treatment temperature of about -304 degrees C, maintaining this treatment temperature for about 24 hours, and then ramping the temperature up to ambient over a period of about eight hours.
5. The proppant of claim 4 wherein the proppant includes nanomaterial.
6. The proppant of claim 1 in which the proppant is cryogenically treated using a piggyback system

7. The proppant of claim 1 wherein cryogenic treatment of the proppant has improved the surface of the proppant.

8. The proppant of claim 1 wherein cryogenic treatment of the proppant has produced microcracks in the proppant.

9. The proppant of claim 1 cryogenically treated to effect for the proppant at least one of: increased strength;, improved shape characteristics; reduced friction; smoother surface; strength and/or shape for reduced fines production; increased sphericity; reduced and/or smoothed sites, areas, locations, or points for anchoring of undesirable materials to a surface of the proppant; improved thermal properties of a material in or on a proppant; improved electrical properties; and improved electrical conductivity of conductive materials in or on a proppant.

10. A method for earth fracturing, the method comprising making a fracture in the earth and emplacing proppant in the fracture, the proppant comprising a cryogenically treated proppant.

11. The method of claim 10 further comprising cryogenically treating the proppant using a piggyback system.

12. A method for cryogenically treating material, the method comprising cryogenically treating the material using a piggyback system.

13. Cryogenically treated nanomaterial.

14. The nanomaterial of claim 13 cryogencially treated with a treatment comprising:
introducing the nanomaterial into a chamber;
ramping the temperature down over a period of about eight hours from ambient to a treatment temperature of about -304 degrees C;
maintaining this treatment temperature for about 24 hours; and then
ramping the temperature up to ambient over a period of about eight hours.

15. The nanoamterial of claim 13 wherein the nanomaterial is one of: coatings, composites, matrices, fabrics, fibers, webs, felts, laminates, nanoparticles, nanotubes, nanostructures, nanocomposites, nanopastes, nanohorns, coated *nanomaterial,* nanomatrices, ceramic nanomatrices, nanoplatlets, nanoflakes, nanoribbons, nanographene, transformed nanomaterial, nanowires, nanorods, nanopillars, nanofibrils, nanospheres, nanobelt, nanosheet, nanocard, nanoprism, quantum dot, quantum wires, carbon nanotubes, single-wall carbon nanotubes (SWNTs), multi-wall carbon nanotubes (MWNTs), double-wall carbon nanotubes (DWNTs), buckytubes, fullerene tubes, tubular fullerenes, graphite fibrils, carbon nanofibers, functionalized nanotubes, graphene, and combinations of two or more of these.

16. The nanomaterial of claim 13 cryogenically treated with a treatment which is one of a SCT and a DCT.

17. The nanomaterial of claim 13 wherein the nanomaterial is formed into a proppant.

18. The nanomaterial of claim 13 in which the nanomaterial is cryogenically treated using a piggyback system.

19. The nanomaterial of claim 13 wherein cryogenic treatment of the nanomaterial has improved a surface of the nanomaterial, withor without microcracks.

20. The nanomaterial of claim 13 cryogenically treated to effect for the nanomaterial at least one of: increased strength;, improved shape characteristics; reduced friction; smoother surface; strength and/or shape for reduced fines production; reduced and/or smoothed sites, areas, locations, or points for anchoring of undesirable materials to a surface of the nanomaterial; improved thermal properties of the nanomaterial; improved electrical properties; and improved electrical conductivity of conductive nanomaterial.

Fig. 1A

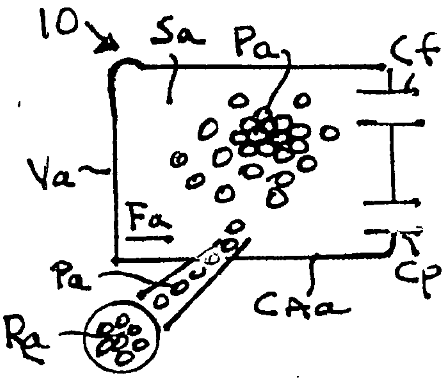


Fig. 1B

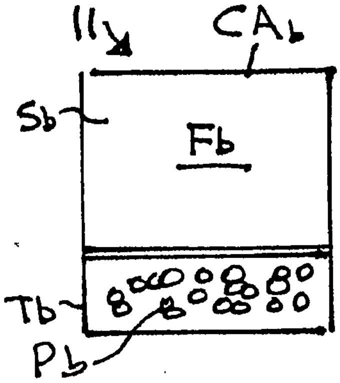


Fig. 1C

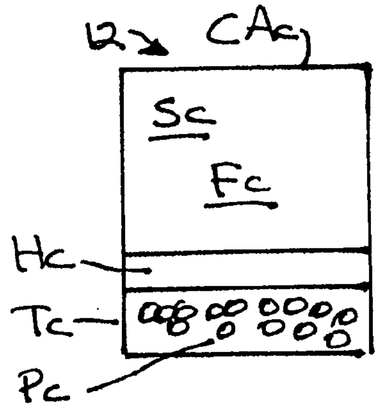


Fig. 2

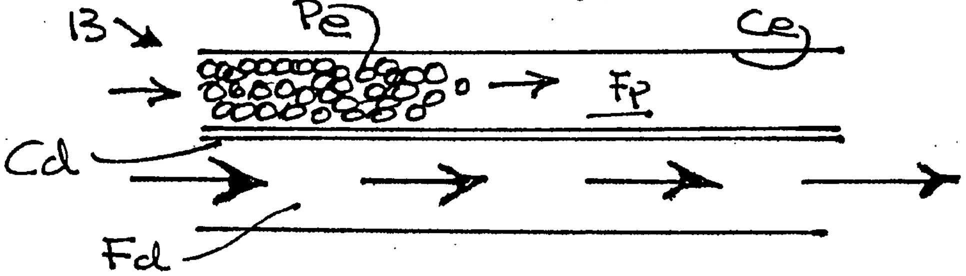
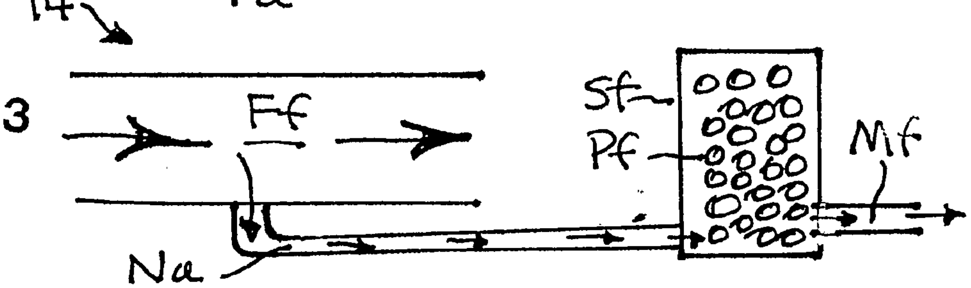


Fig. 3



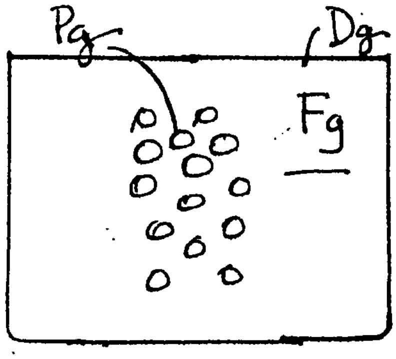


Fig. 4A

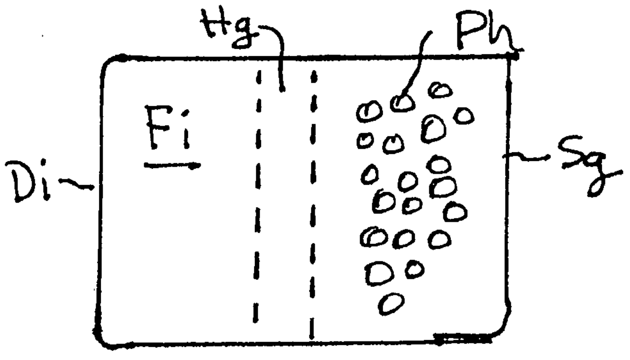


Fig. 4B

Fig. 5

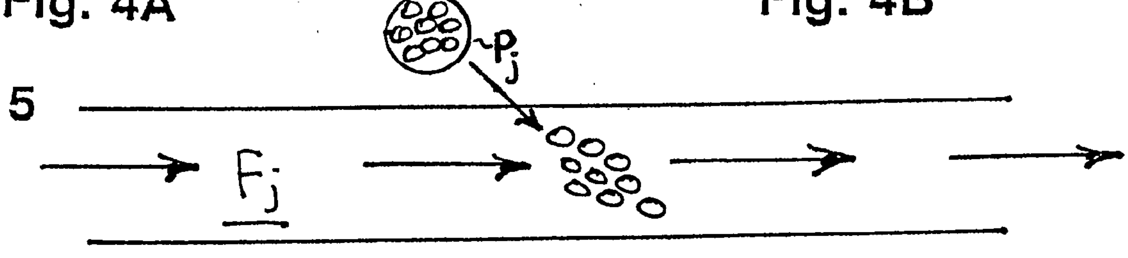
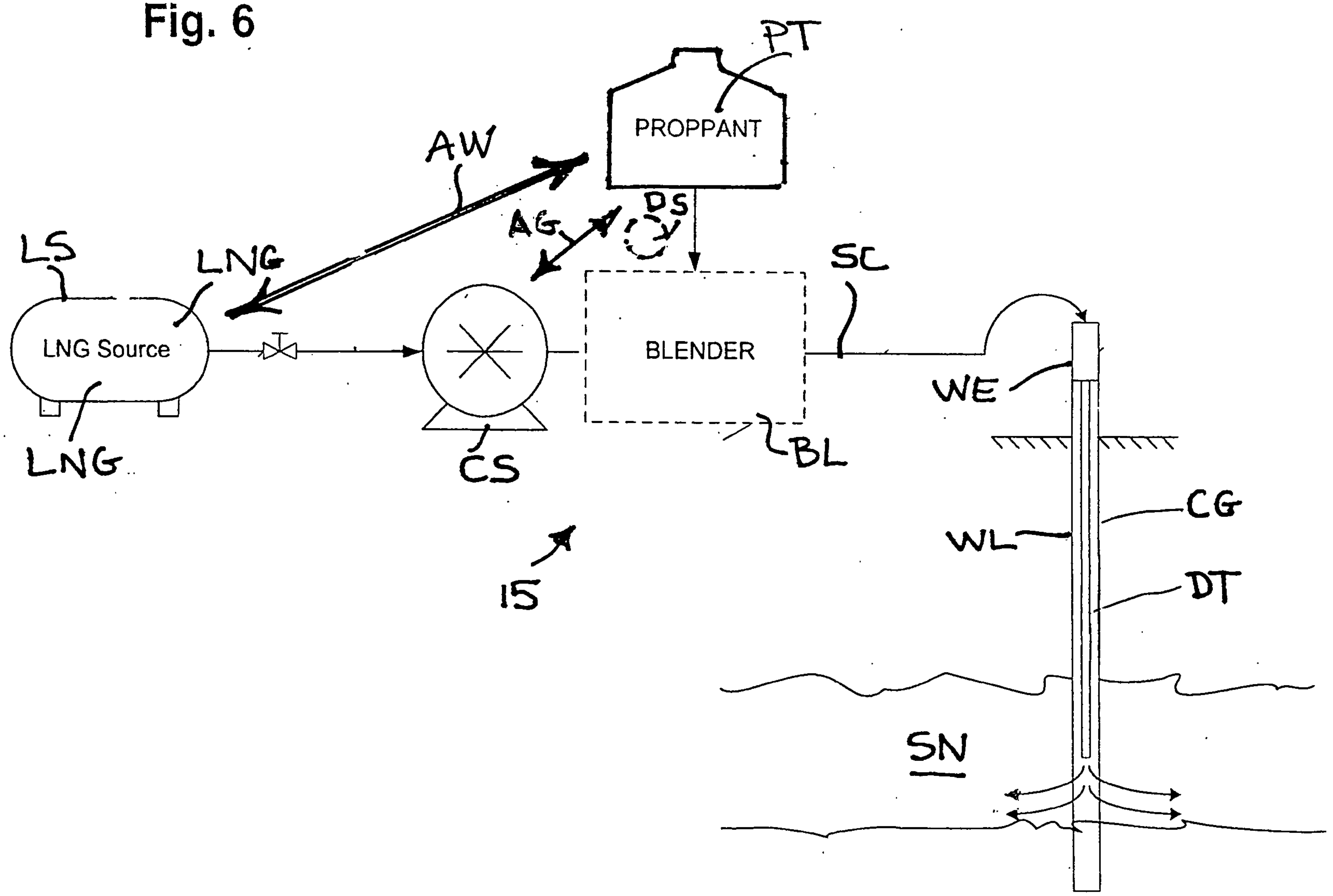


Fig. 6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AW
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LS
LNG
LNG Source
LNG
SC
BLENDER
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CS
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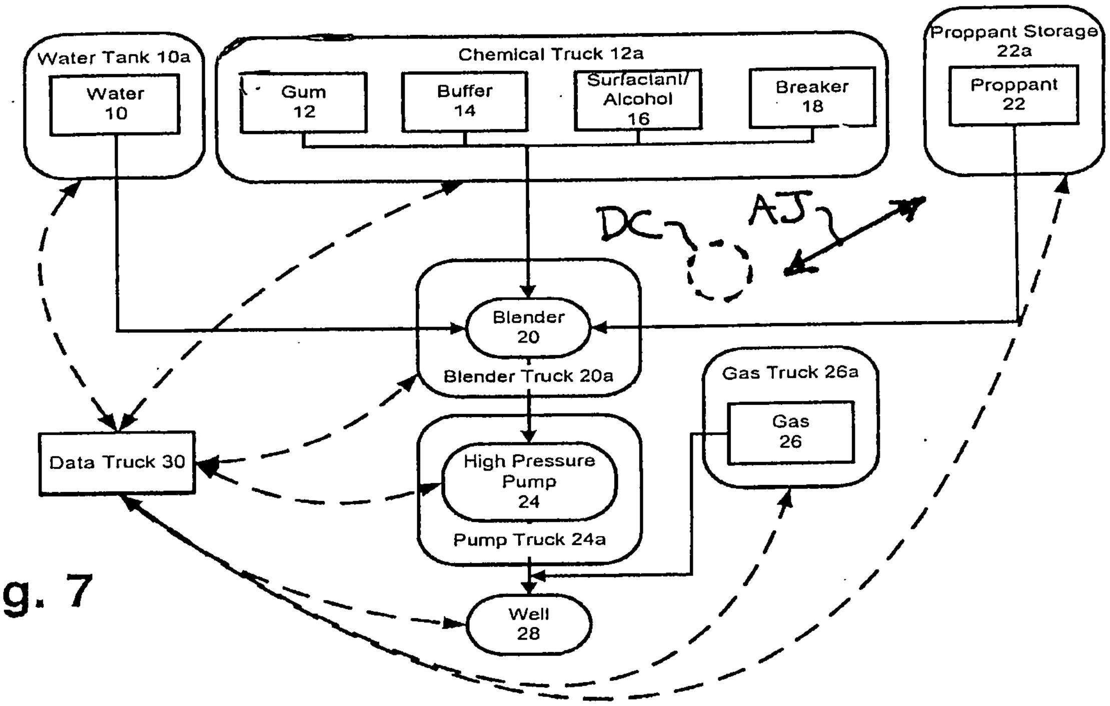
WL
15
DT
SN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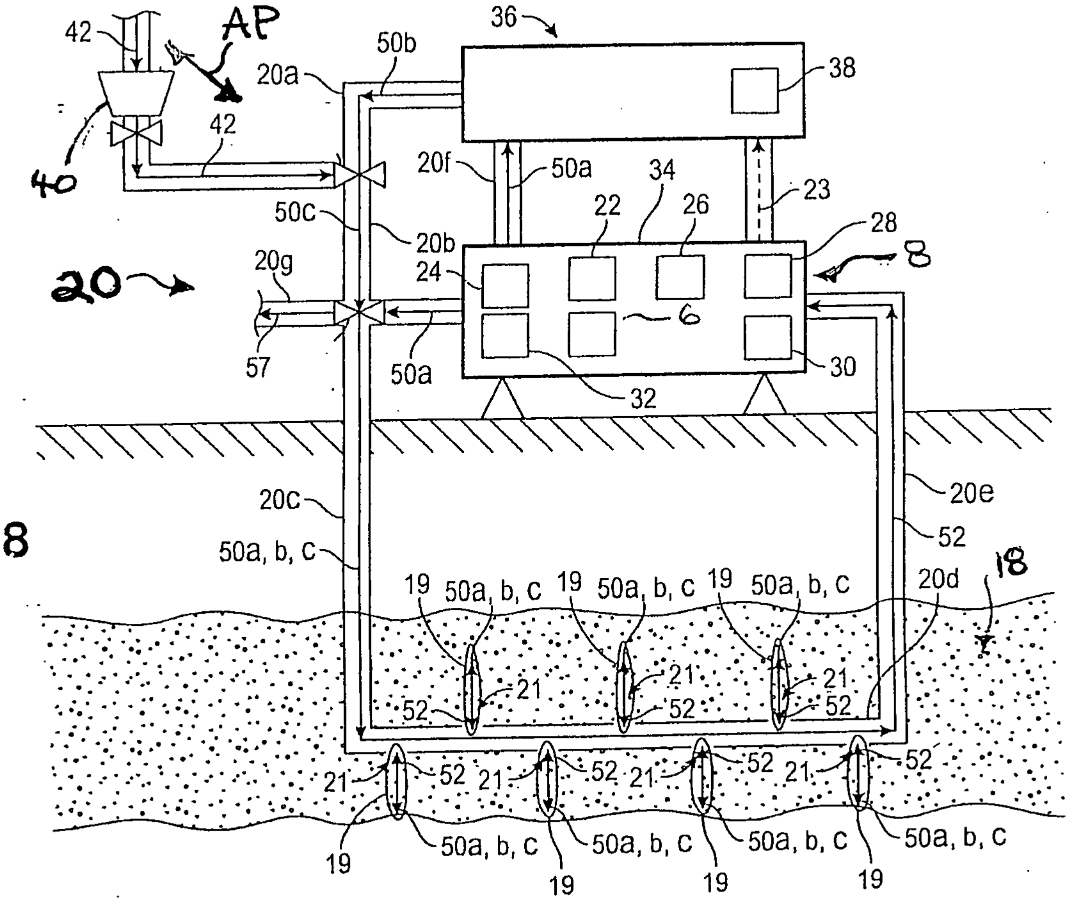
Water 10
Chemical Truck 12a
Gum 12
Buffer 14
Surfactant/ Alcohol 16
Breaker 18
Proppant Storage 22a
Proppant 22
DC
AJ
Blender 20
Blender Truck 20a
Gas Truck 26a
Gas 26
Data Truck 30
High Pressure Pump 24
Pump Truck 24a
Well 28

Fig. 7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20g
24
6
57
50a
32
30
20c
20e
50a, b, c
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18
19
50a, b, c
20d
21
52
19
50a, b, c

Fig. 8

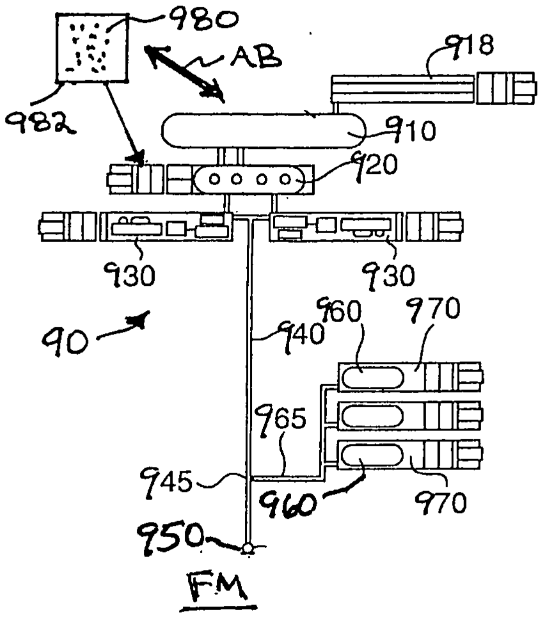

Fig. 9

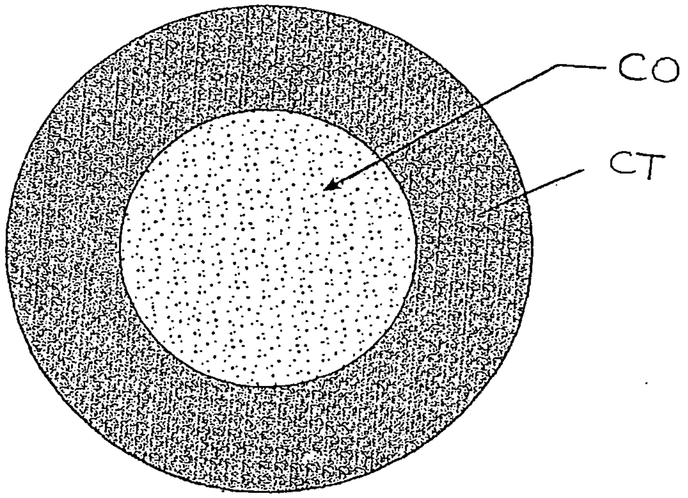

Fig. 10

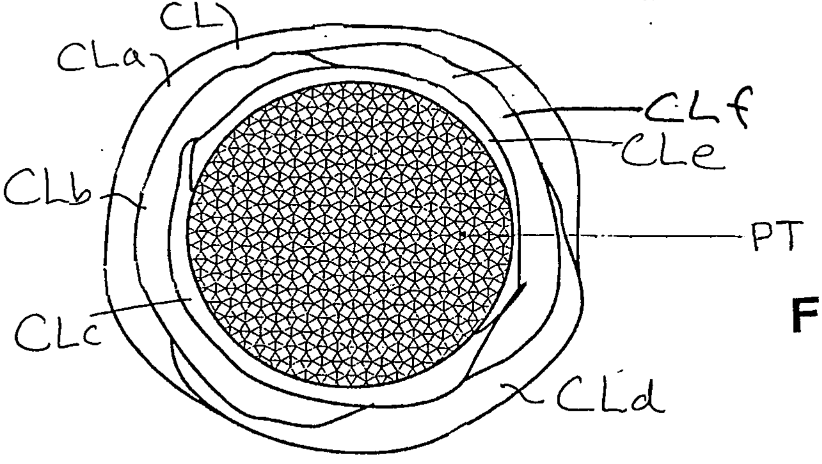

Fig. 11

Fig. 12A

Fig. 12B

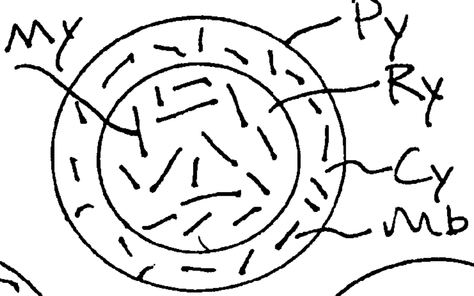

Fig. 12C

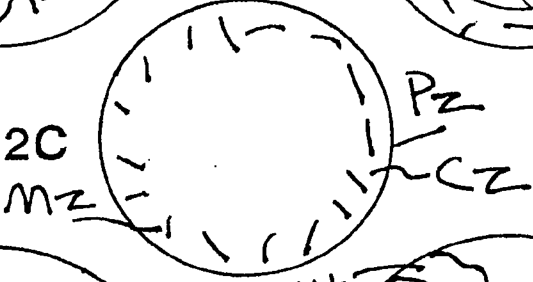

Fig. 12D

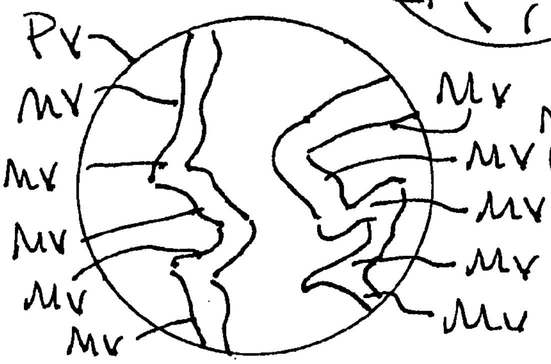

Fig. 13A

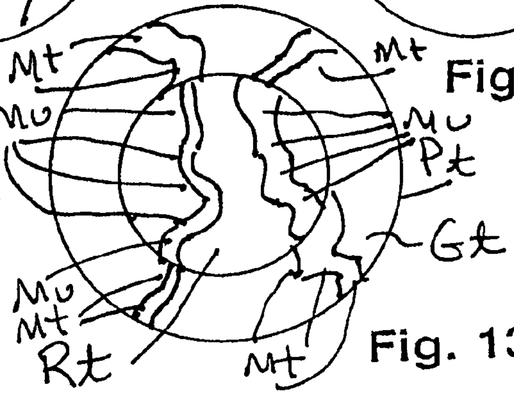

Fig. 13B

Fig. 14A

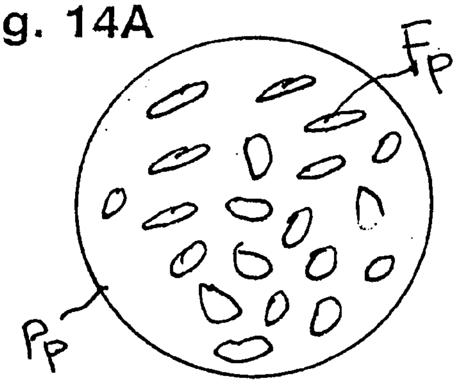

Fig. 14B

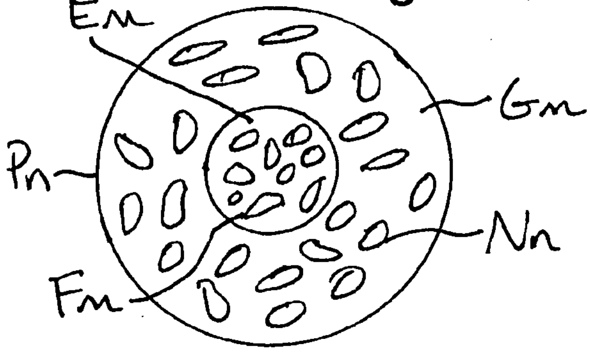

Fig. 15

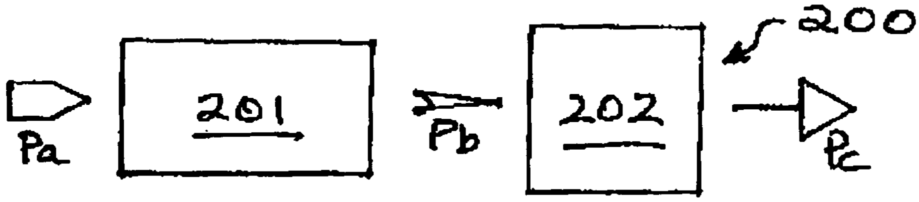

Fig. 16A

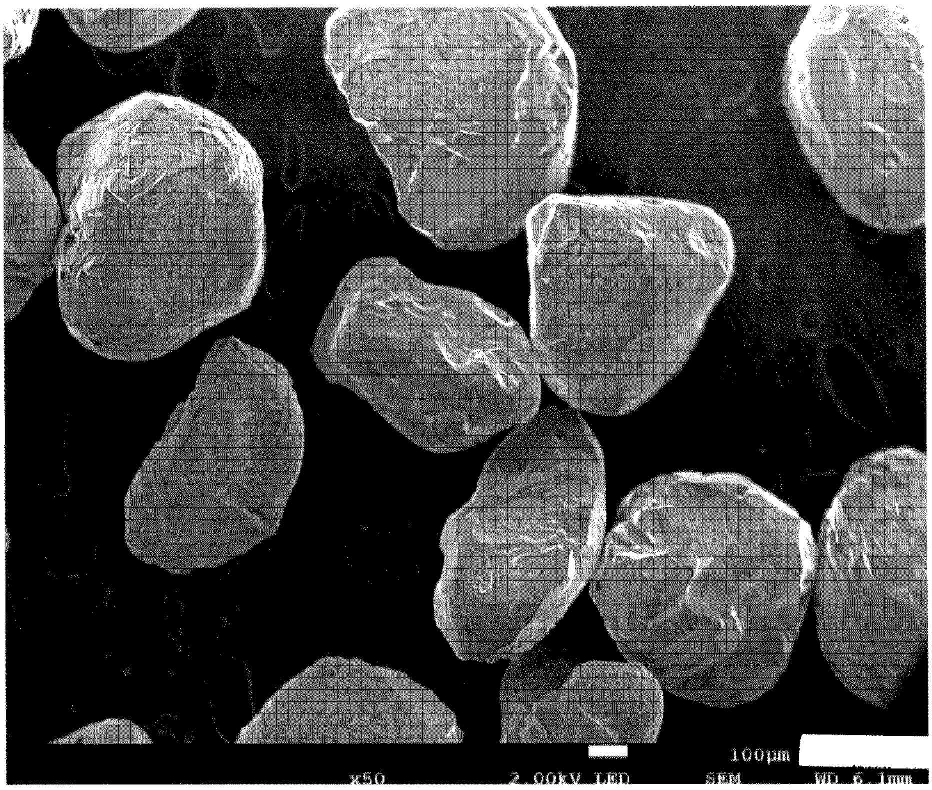

Fig. 16B

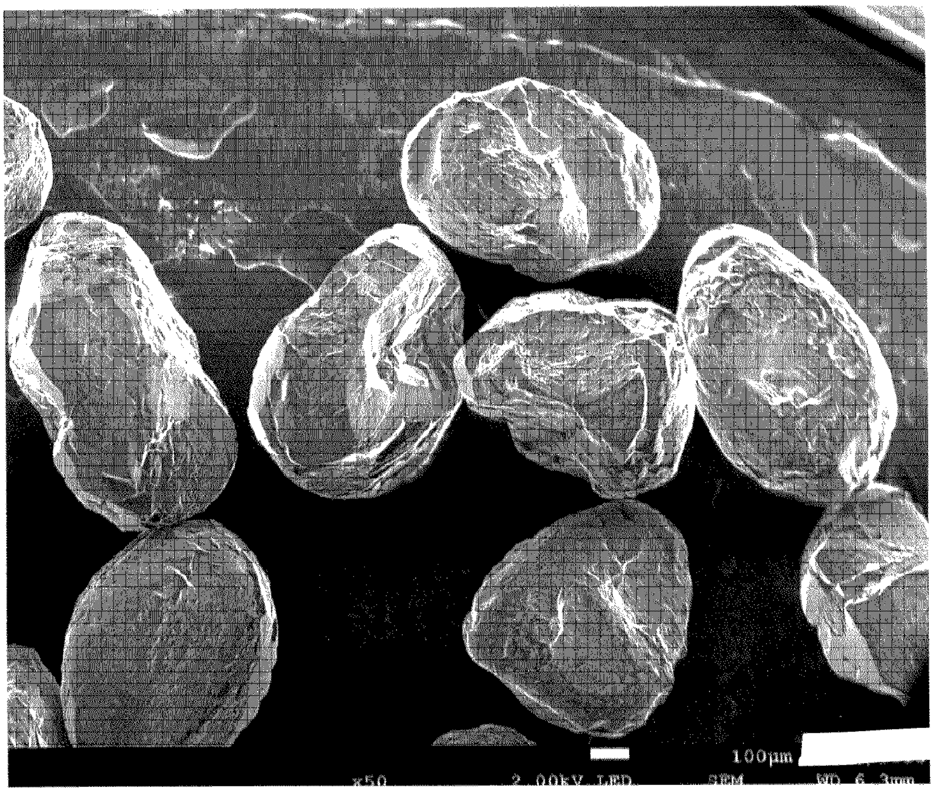

Fig. 17A

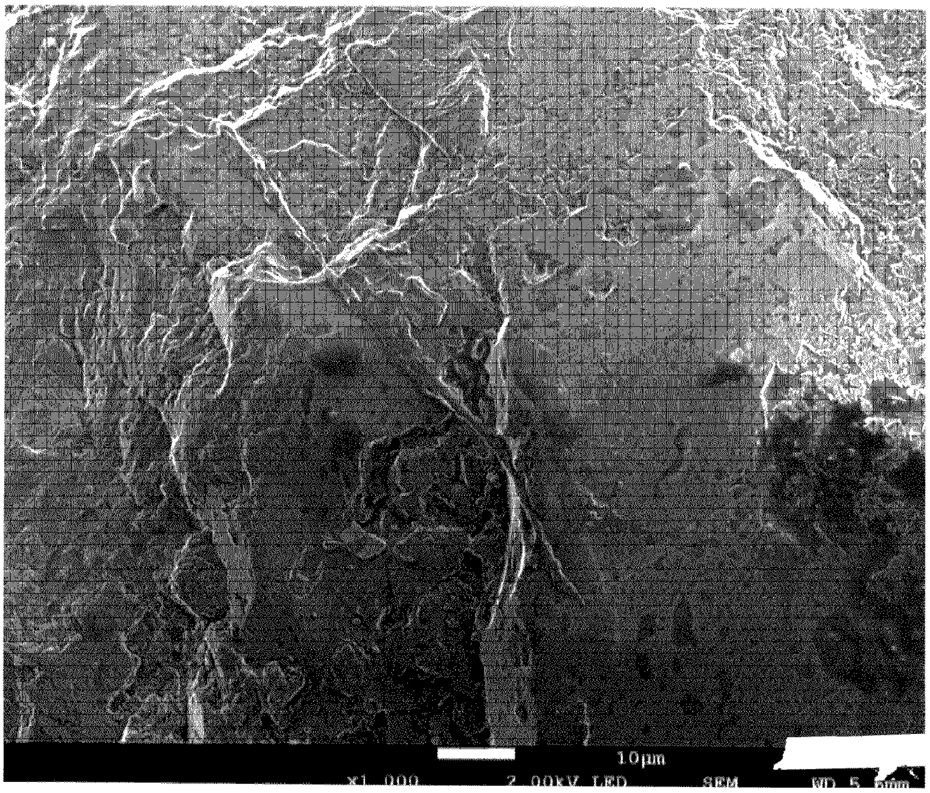

Fig. 17B

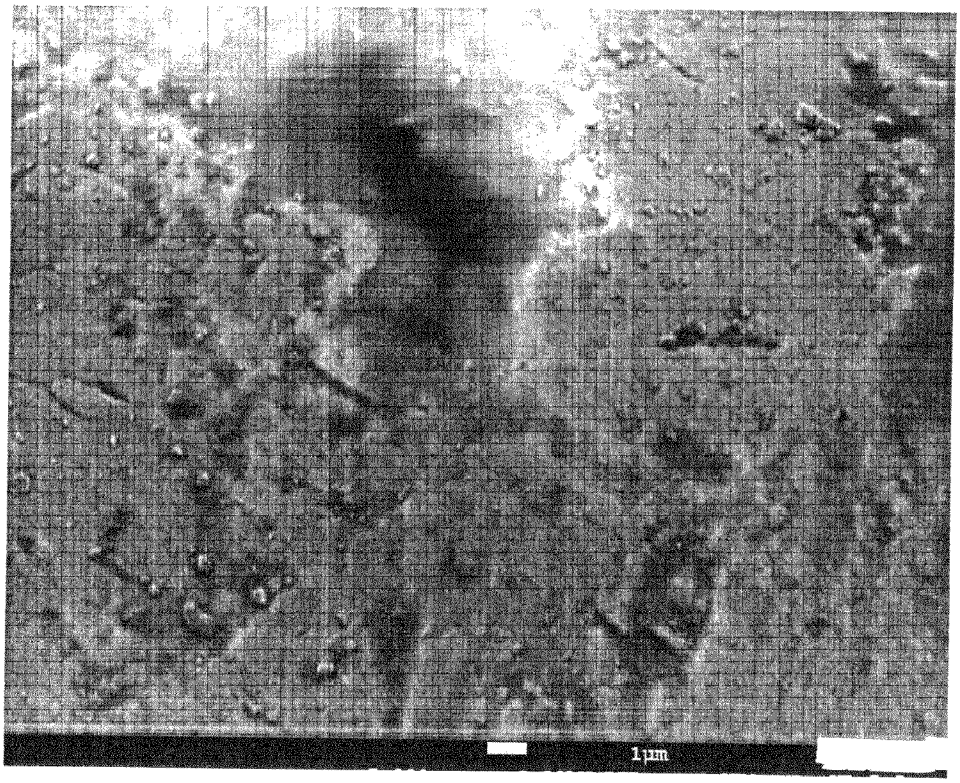

Fig. 17C

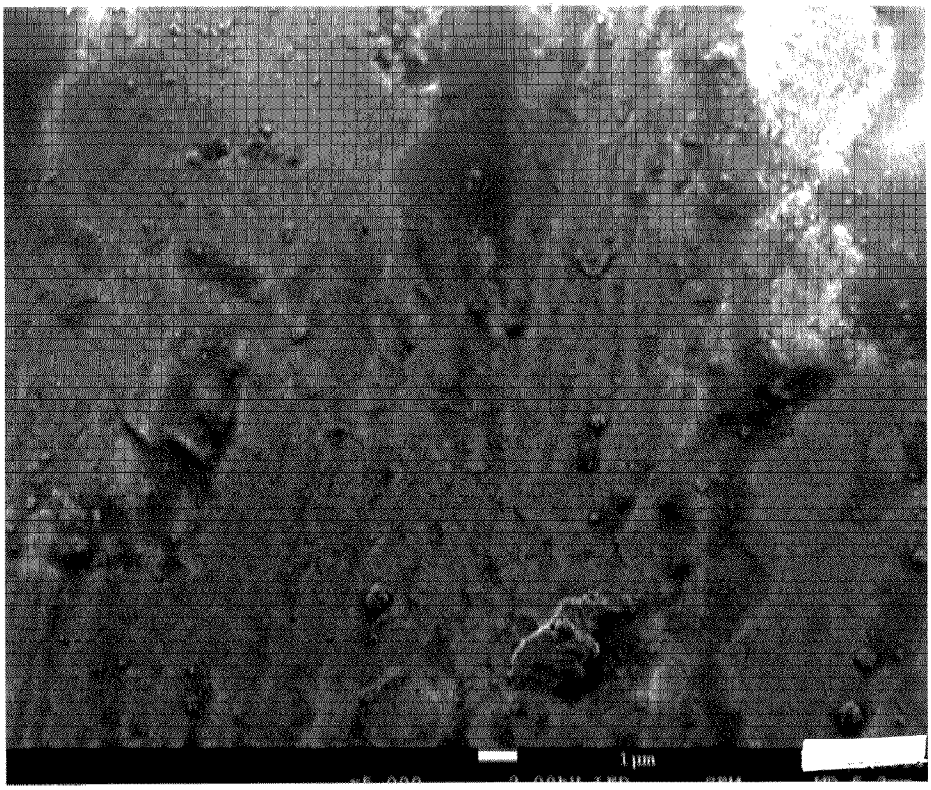

Fig. 18A

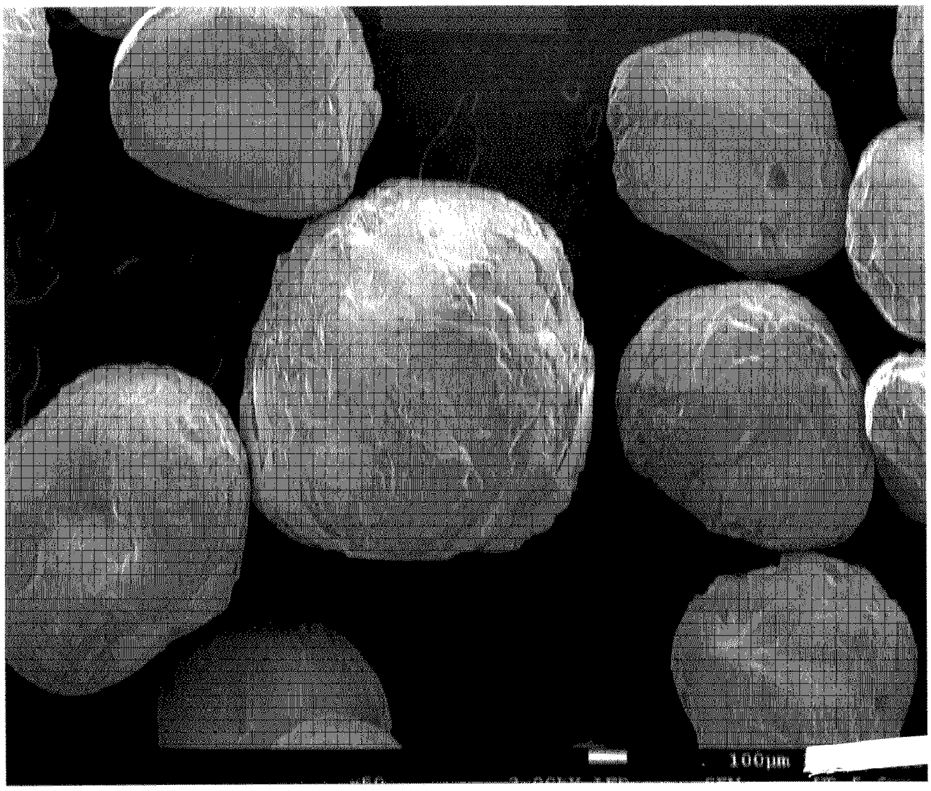

Fig. 18B

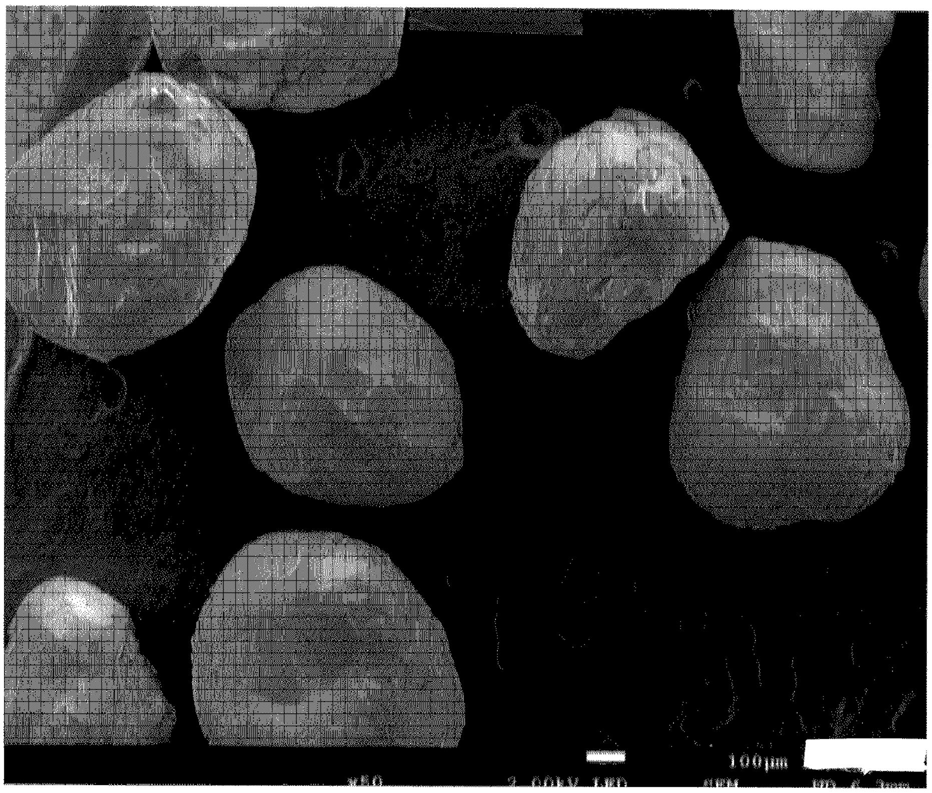

Fig. 18C

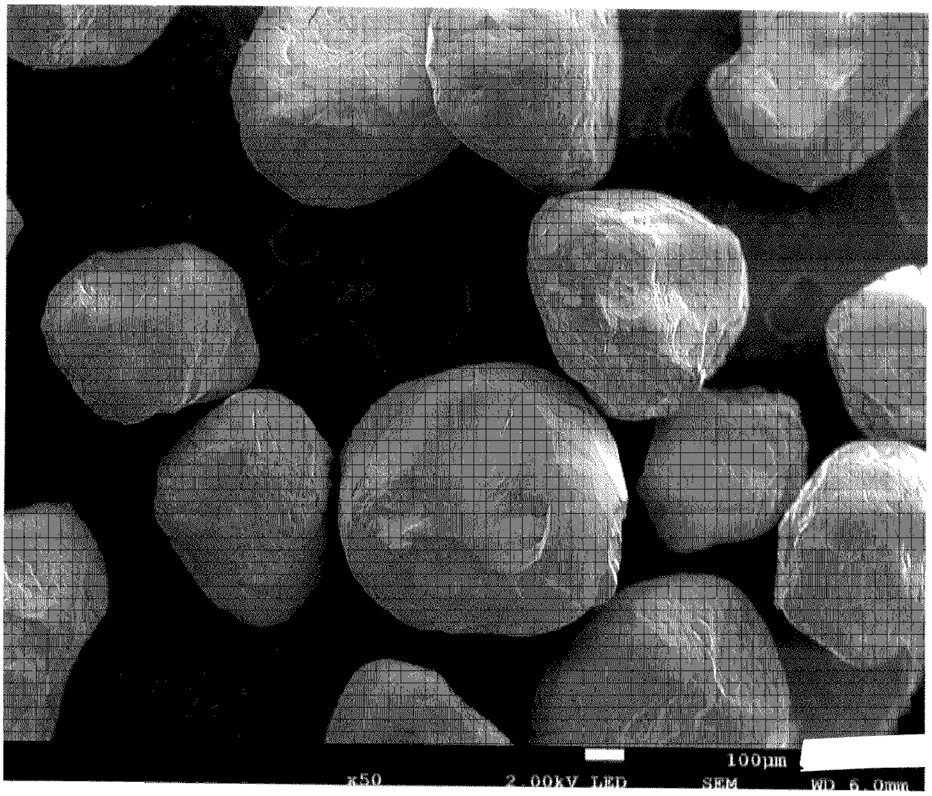

Fig. 19A

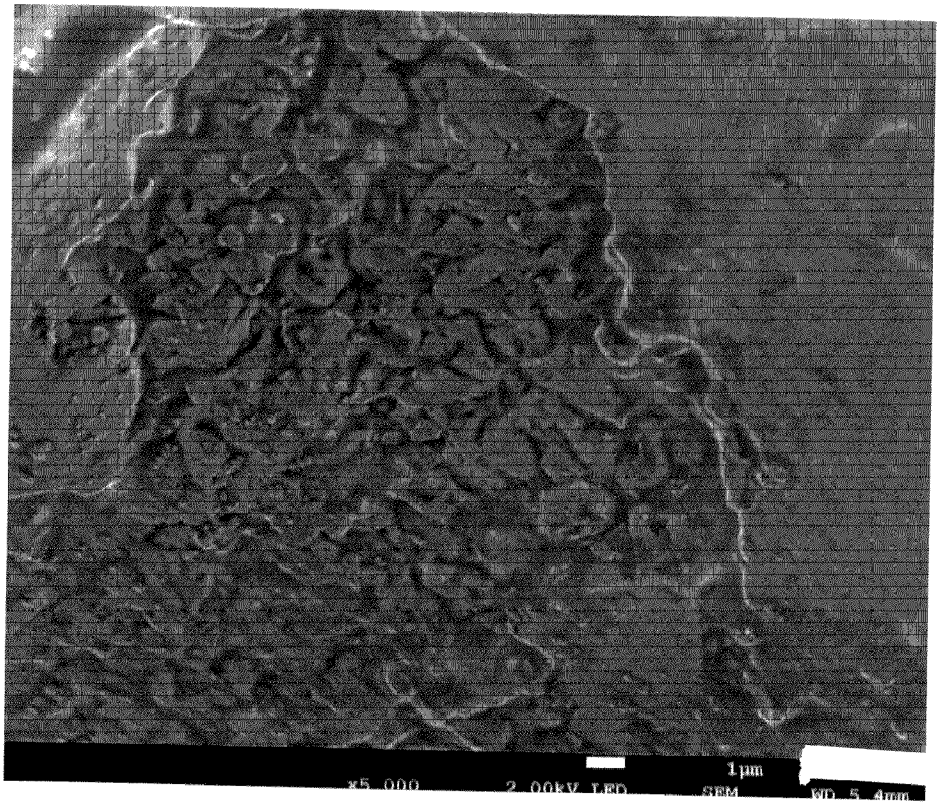

Fig. 19B

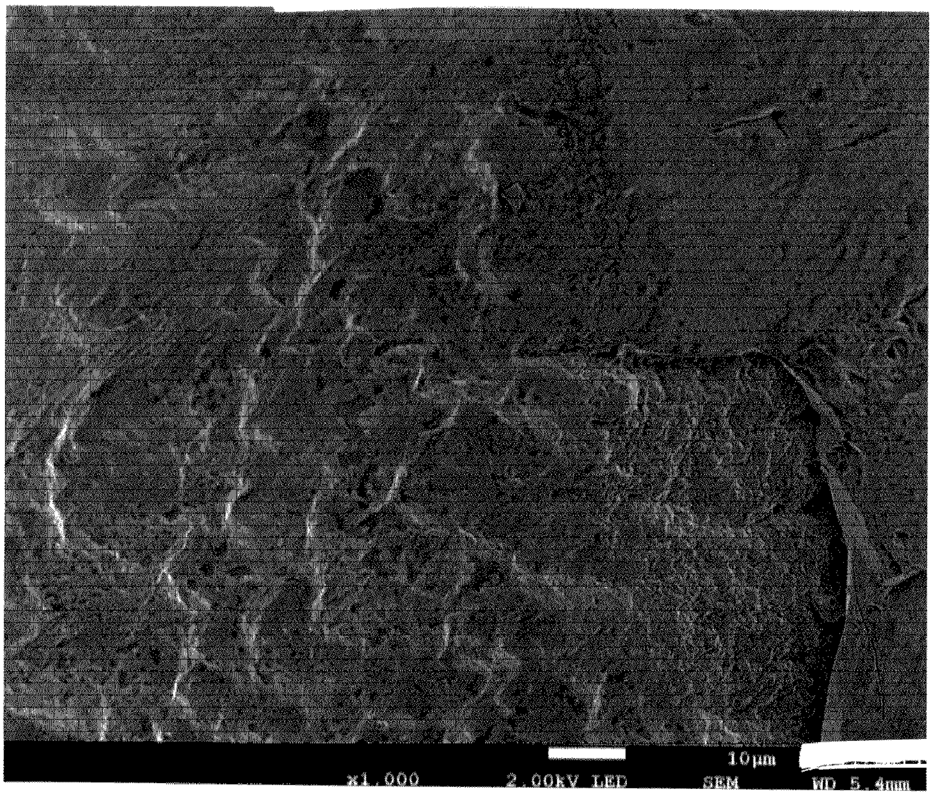

Fig. 20A

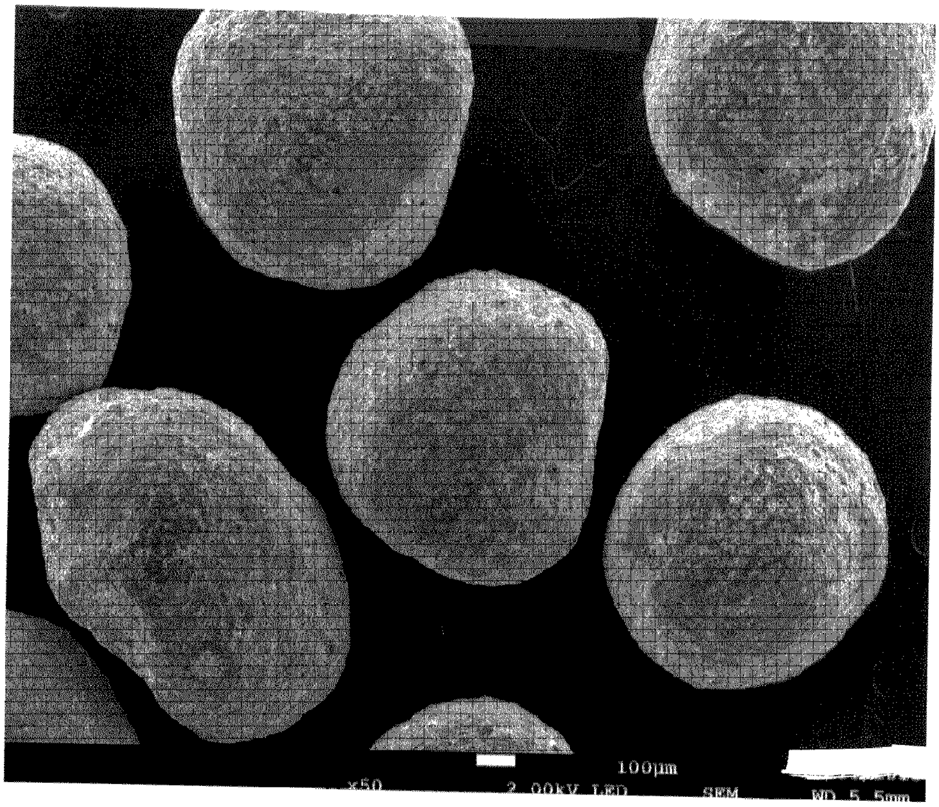

Fig. 20B

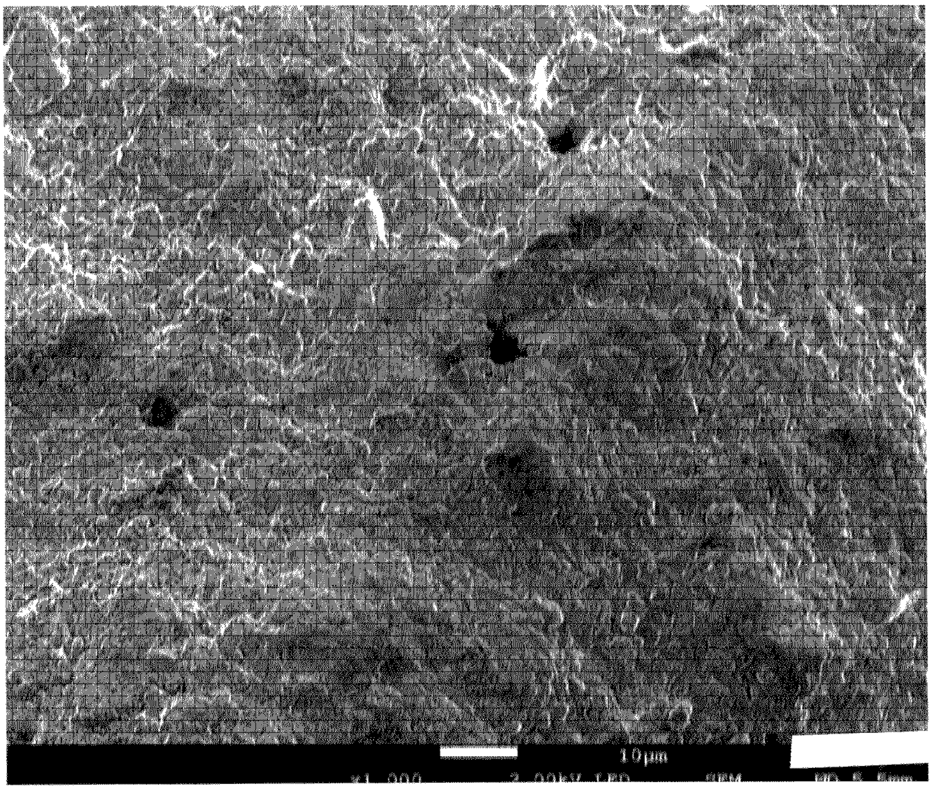

Fig. 20C

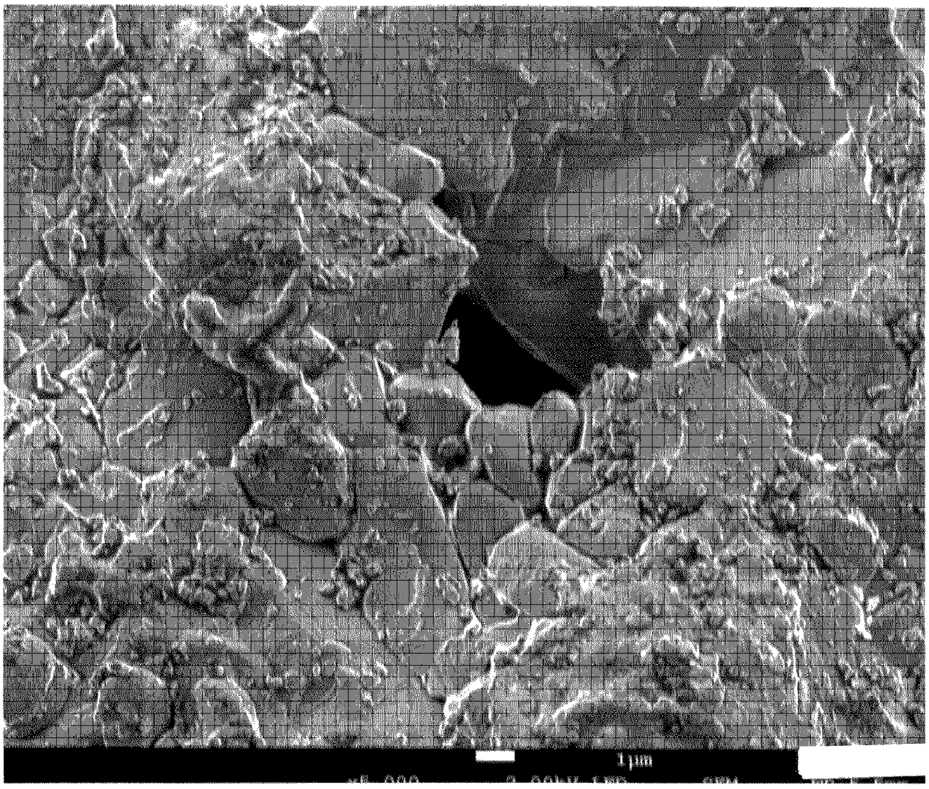

Fig. 21A

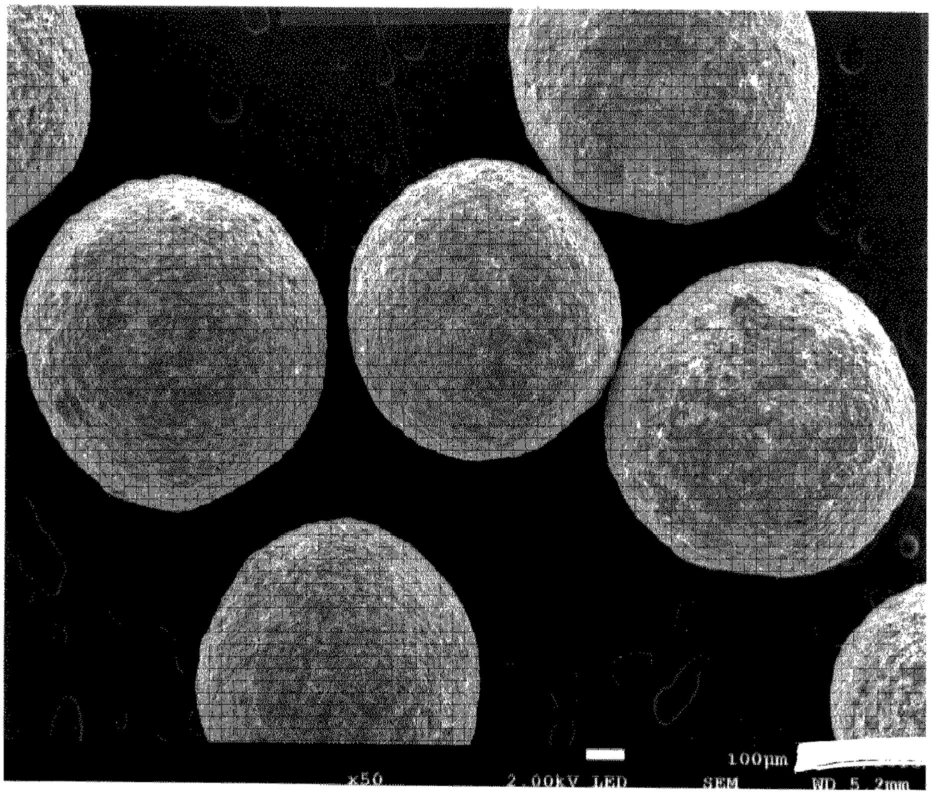

Fig. 21B

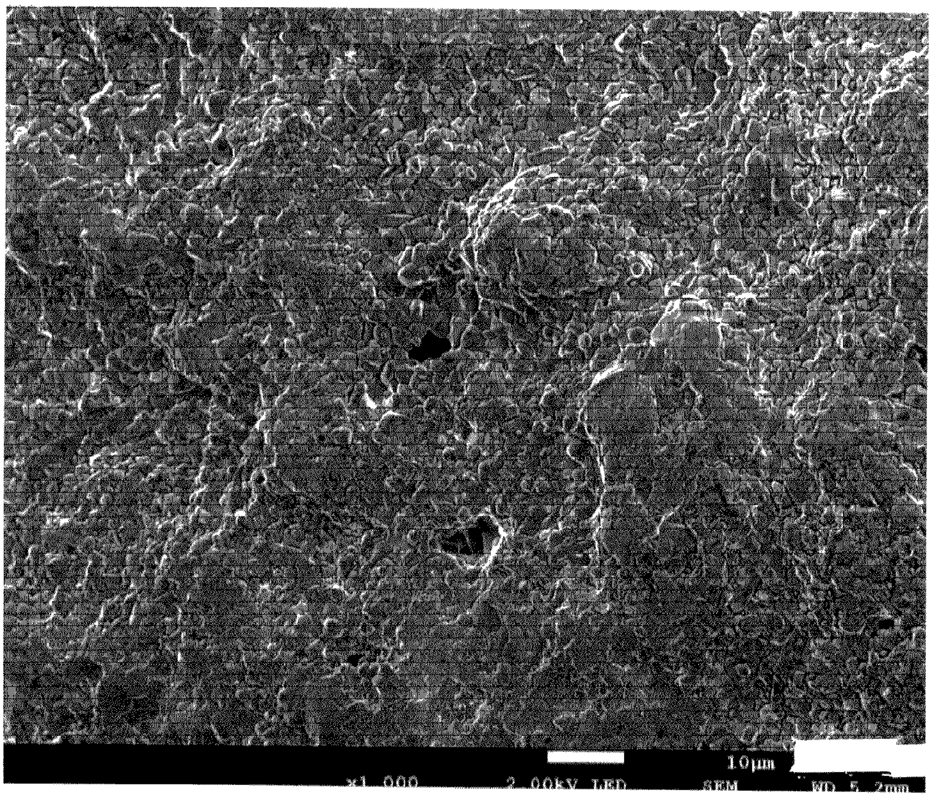

Fig. 21C

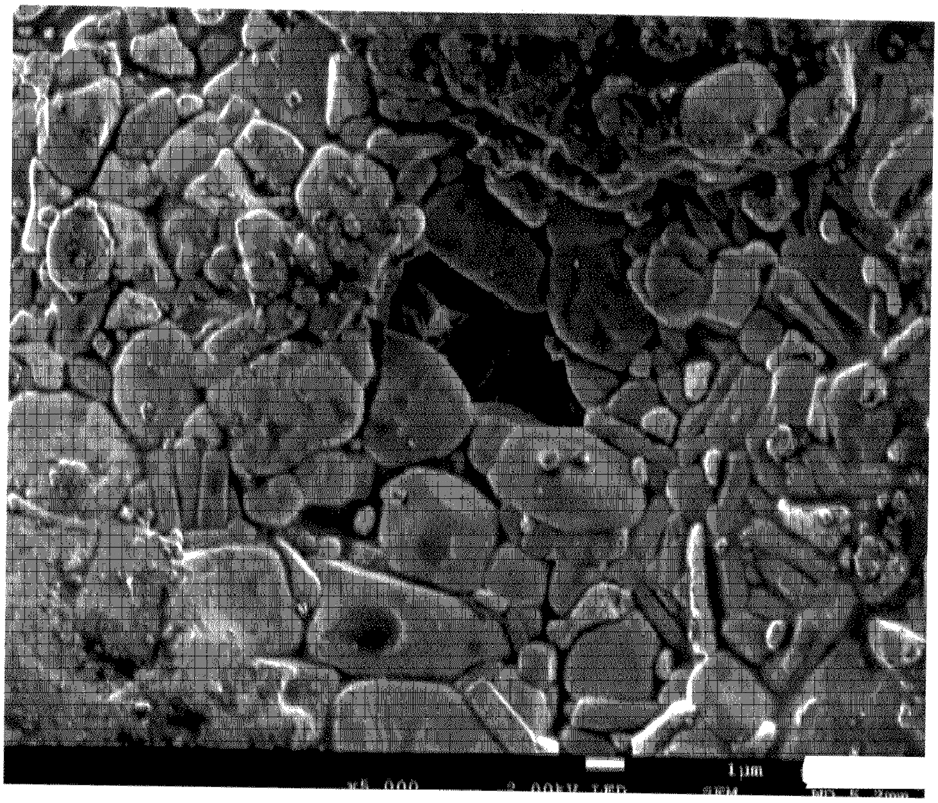

Fig. 22

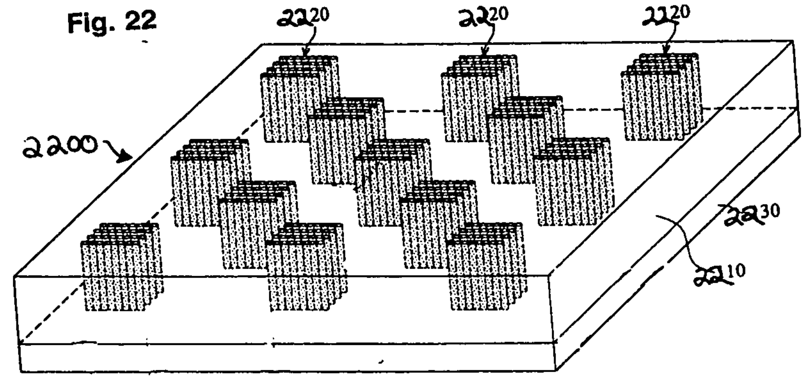

Fig. 23

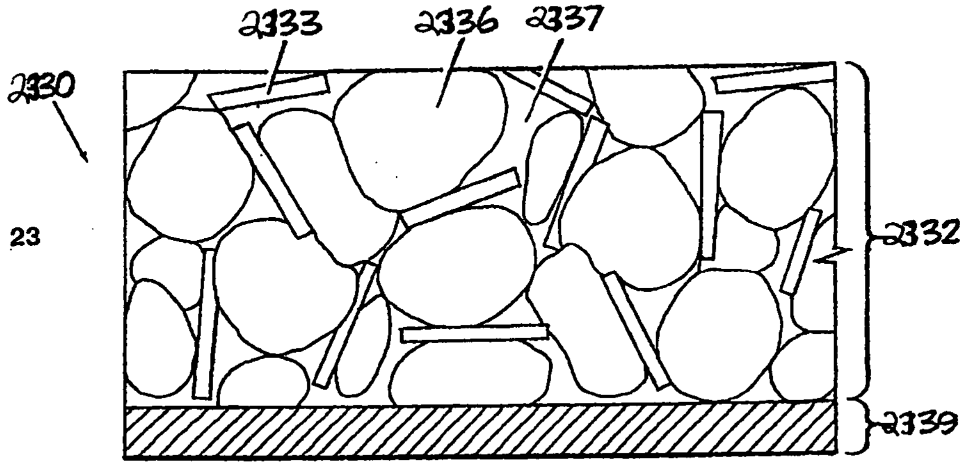

Fig. 24A

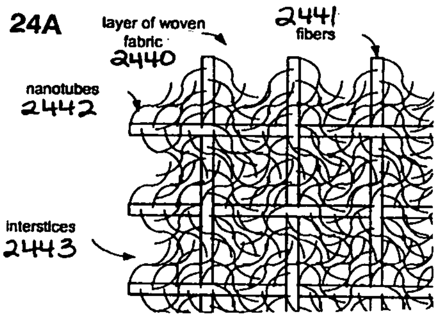

Fig. 24B

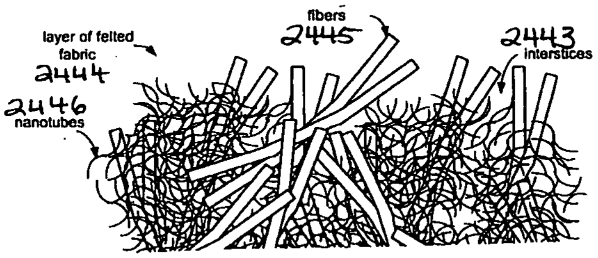

Fig. 24C