US 20080179057A1

(19) **United States**

(12) **Patent Application Publication**

Dawson

(10) **Pub. No.: US 2008/0179057 A1**

(43) **Pub. Date: Jul. 31, 2008**

(54) WELL TREATING AGENTS OF METALLIC SPHERES AND METHODS OF USING THE SAME

(75) Inventor: **Jeffrey C. Dawson**, Spring, TX (US)

Correspondence Address:
JONES & SMITH , LLP
2777 ALLEN PARKWAY, SUITE 800
HOUSTON, TX 77019

(73) Assignee: **BJ Services Company**

(21) Appl. No.: **12/018,050**

(22) Filed: **Jan. 22, 2008**

Related U.S. Application Data

(60) Provisional application No. 60/897,679, filed on Jan. 26, 2007.

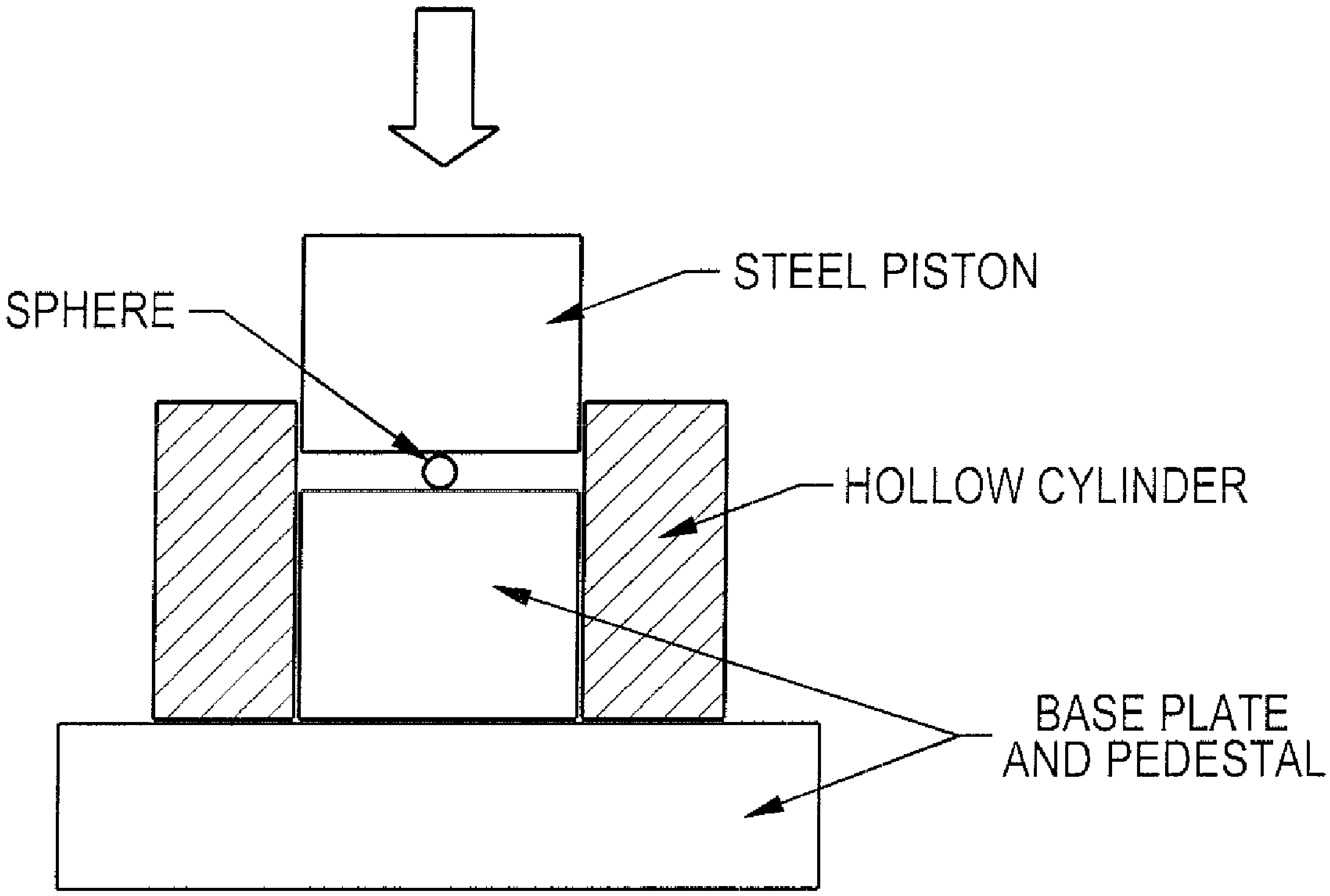
Publication Classification

(51) **Int. Cl.**
E21B 43/267 (2006.01)

(52) **U.S. Cl.** **166/280.2**; 507/220; 507/204

(57) **ABSTRACT**

Hollow non-porous metallic spheres may be used in treatment of subterranean formations, including hydraulic fracturing and sand control methods, such as gravel packing. The spheres typically having a diameter ranging from about 4 mesh to about 100 mesh. When employed in deep water environments having high closure stresses, the spheres have a thicker wall and are characterized by the higher ASG, typically between 2.5 to about 4.0. The ASG of the spheres, when less harsh environments are encountered, is generally ultra lightweight (ULW) with an ASG less than or equal to 2.0. Fracture conductivity may be increased by the placement of the hollow non-porous metallic spheres as a partial monolayer.



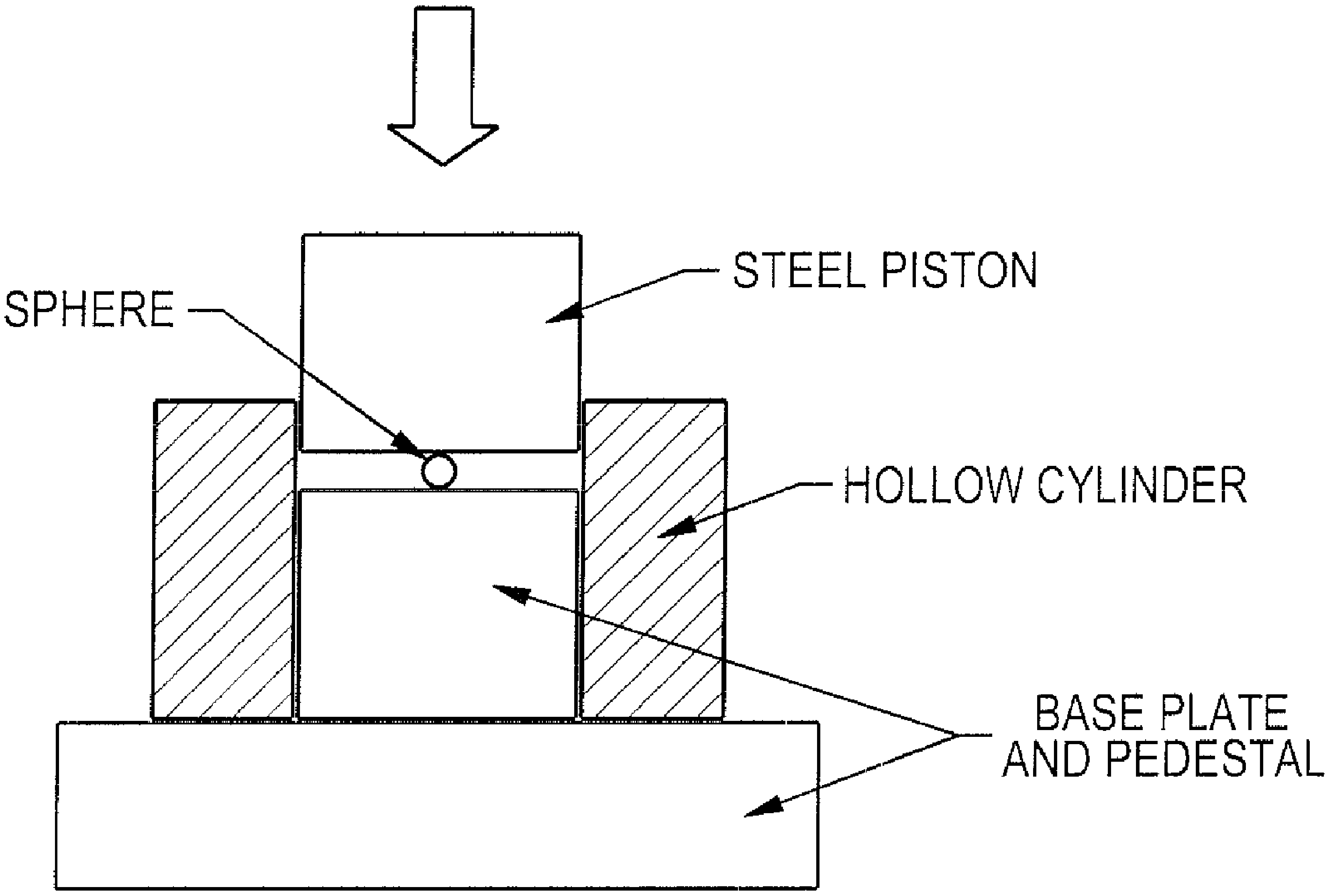

STEEL PISTON
SPHERE
HOLLOW CYLINDER
BASE PLATE AND PEDESTAL

FIG. 1

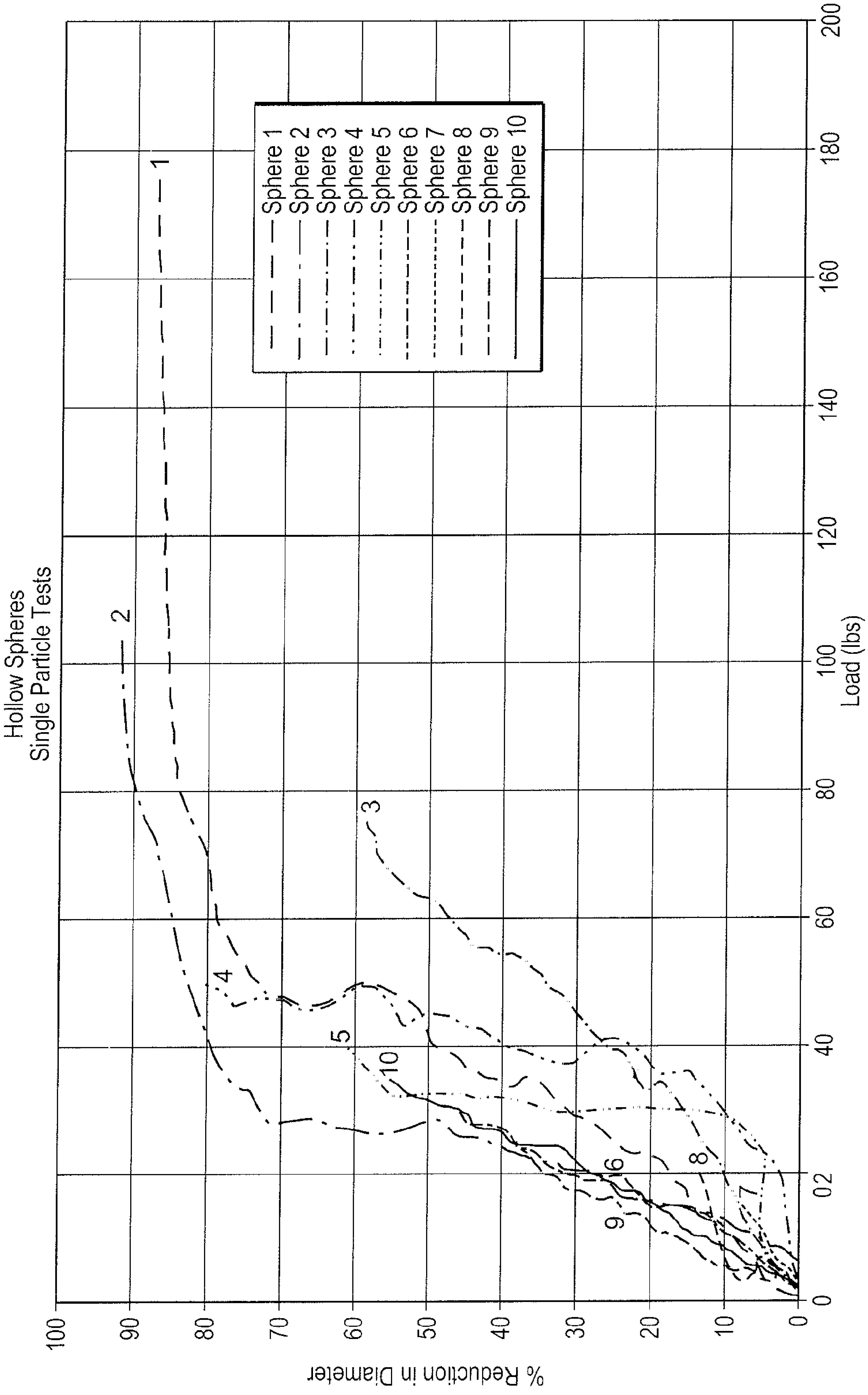
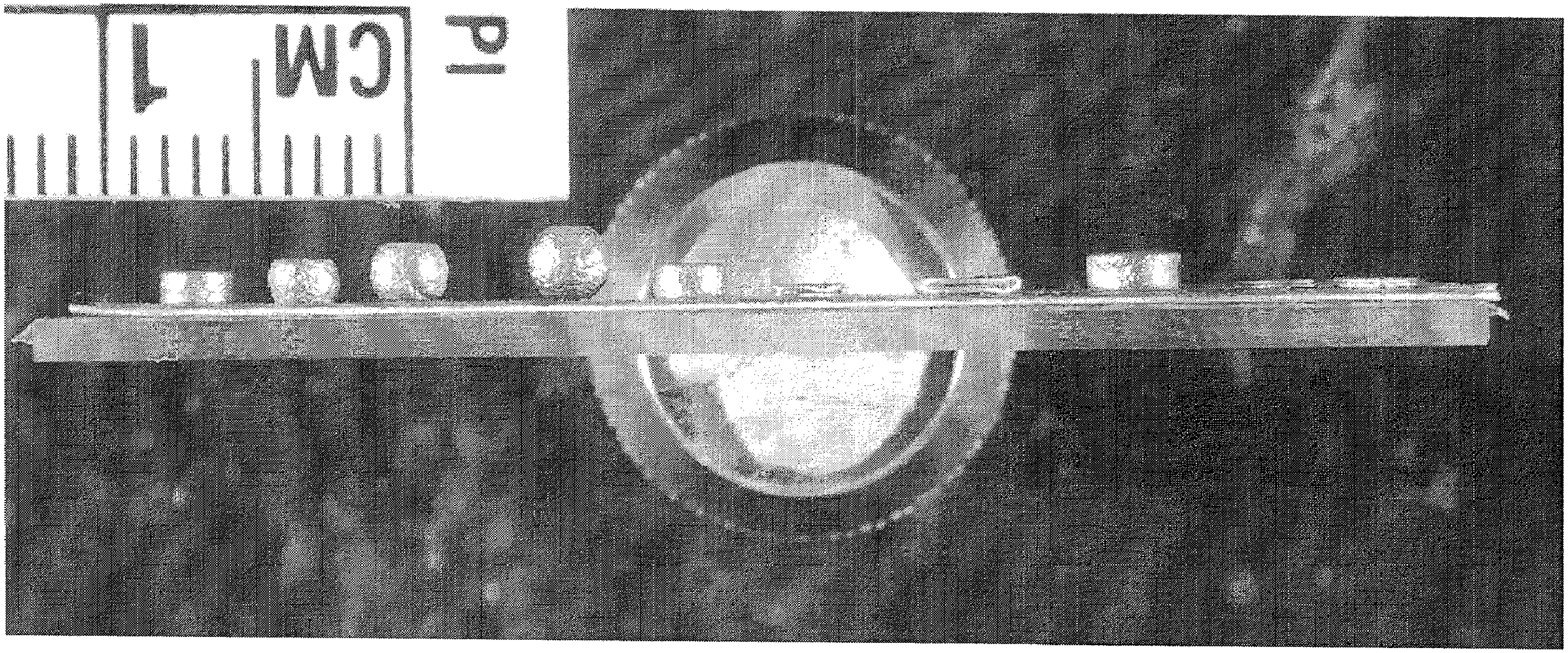

Hollow Spheres
Single Particle Tests
% Reduction in Diameter
0
10
20
30
40
50
60
70
80
90
100
Load (lbs)
0
20
40
60
80
100
120
140
160
180
200
Sphere 1
Sphere 2
Sphere 3
Sphere 4
Sphere 5
Sphere 6
Sphere 7
Sphere 8
Sphere 9
Sphere 10
1
2
3
4
5
6
7
8
9
10

FIG. 2



Sample	10	9	8	7	6	5	4	3	2	1
Force	35 lb	25 lb	20 lb	15 lb	30 lb	40lb	50 lb	75 lb	100 lb	175 lb
Init. Dia.	2.34mm	2.26mm	2.44mm	2.54mm	2.32mm	2.24mm	2.79mm	2.86mm	2.18mm	2.32mm
Final Thck	1.06mm	1.42mm	1.89mm	2.45mm	1.20mm	0.04mm	0.57mm	1.23mm	0.19mm	0.31mm

FIG. 3

WELL TREATING AGENTS OF METALLIC SPHERES AND METHODS OF USING THE SAME

[0001] This application claims the benefit of U.S. patent application Ser. No. 60/897,679, filed on Jan. 26, 2007, wherein is herein incorporated by reference.

FIELD OF THE INVENTION

[0002] This invention relates to methods and compositions useful for subterranean formation treatments, such as hydraulic fracturing and sand control. In particular, this invention relates to the use of hollow substantially non-porous metallic spheres in sand control methods such as gravel packing, frac pack treatments, etc., as well as proppant material in hydraulic fracturing.

BACKGROUND OF THE INVENTION

[0003] Stimulation procedures often require the use of well treating materials having high compressive strength. In hydraulic fracturing, such materials must further be capable of enhancing the production of fluids and natural gas from low permeability formations.

[0004] In a typical hydraulic fracturing treatment, fracturing treatment fluid containing a solid proppant material is injected into the wellbore at high pressures. Once natural reservoir pressures are exceeded, the fluid induces fractures in the formation and proppant is deposited in the fracture, where it remains after the treatment is completed. The proppant material serves to hold the fracture open, thereby enhancing the ability of fluids to migrate from the formation to the wellbore through the fracture. Fractured well productivity depends on the ability of a fracture to conduct fluids from a formation to a wellbore. Fracture conductivity is an important parameter in determining the degree of success of a hydraulic fracturing treatment. Choosing a proppant is critical to the success of well stimulation.

[0005] Conventional proppants, such as sand and glass beads and bauxite, as well as resin-coated sands, intermediate strength ceramics and sintered bauxite, are characterized by a fairly high apparent specific gravity (ASG). For instance, the ASG for sand is about 2.65 and the ASG for sintered bauxite is 3.4. Proppant transport is often difficult with such proppants. Further, higher ASG proppants (greater than 2.65) often cause a reduction in propped fracture volume, based on equivalent mass of proppant, which, in turn, causes a reduction in fracture conductivity. The high ASG of such conventional proppants is known to be the controlling factor in the difficulties in proppant transport and reduced propped fracture volume.

[0006] More recently, ultra lightweight (ULW) materials have been used as proppants. ULW proppants are typically characterized by an ASG less than or equal to 2.45 and exhibit better deformability than conventional heavy proppants. ULW proppants, in addition to having lower ASG than conventional heavy proppants, typically exhibit sufficient strength to withstand the rigors of high temperatures and high stresses downhole. While offering excellent compressive strength, ULW proppants often soften and loose their compressive strength especially at high temperature and high pressure downhole conditions. Alternatives have therefore been sought.

[0007] Further, alternative materials have been sought for use with hydraulic fracturing fluids (such as water, salt brine and slickwater) at relatively low concentrations in order that a partial monolayer of proppant in the fracture may be obtained. In conventional sand packs, tightly held packs often are characterized by insufficient interconnected interstitial spaces between abutting particulates. Increased interstitial spaces between the particulates are typically desired in order to increase conductivity. This may be achieved by use of a partial monolayer fracture wherein reduced volume of proppant particulates in a fracture is created by the use of widely spaced proppant particulates. Increased fracture conductivity results since the produced fluids typically flow around the widely-spaced proppant particulates rather than through the interstitial spaces in a packed bed. The phenomena of partial monolayer fracturing has been discussed in the literature. See, for instance, Brannon et al, "Maximizing Fracture Conductivity with Partial Monolayers: Theoretical Curiosity or Highly Productive Reality" SPE 90698, presented at the SPE Annual Technical Conference and Exhibition, Houston, Sep. 26-29, 2004. Unfortunately, partial monolayer fracturing has been difficult to achieve with state-of-the-art proppants.

[0008] Improved well treating agents have also been sought for use in the prevention of sand grains and/or other formation fines from migrating into the wellbore. When such migration occurs, such grains and fines typically reduce the rate of hydrocarbon production from the well. In addition, such grains and fines can cause serious damage to well tubulars and to well surface equipment.

[0009] Gravel packs are often used to control migration of particulates in such producing formations. A gravel pack typically consists of a uniformly sized mass of spherical particulates which are packed around the exterior of a screening device. Such screening devices, typically positioned in an open hole or inside the well casing, have very narrow openings which are large enough to permit the flow of formation fluid but small enough to allow the particulates to pass through. The particulates operate to trap, and thus prevent the further migration of, formation sand and fines which would otherwise be produced along with the formation fluid.

[0010] In order to be useful in gravel packing applications, such particulates must exhibit high strength and be capable of functioning in low permeability formations. ULW well treating agents have been proposed for use in gravel packing applications to improve transport, placement, and packing efficiency. Concerns exist however that ULW particulates do not demonstrate the chemical resistance properties required of particulates for use in gravel packing.

[0011] Alternative well treating agents have therefore been sought which exhibit high compressive strength and which may be used to improve packing efficiency, transport and placement of proppant in fracturing. It is further desired that such materials be useful in other oilfield treatment processes, such as sand control.

SUMMARY OF THE INVENTION

[0012] The invention relates to a well treating agent composed of hollow non-porous metallic spheres. The invention further relates to a well treating composite which contains the hollow non-porous metallic spheres. In a preferred embodiment, the composite consists of a core comprising the metallic spheres and a coating applied onto at least a portion of the hollow non-porous metallic spheres.

[0013] The metallic spheres are preferably composed of stainless steel alloy or carbon steel as well as metals, such as iron, chromium, titanium, nickel, cobalt, aluminum or molybdenum or an alloy mixture of such metals. In a preferred embodiment, the metal is stainless steel or titanium. Typically, the diameter of the spheres ranges from about 4 mesh to about 100 mesh.

[0014] The hollow non-porous metallic spheres are generally introduced into the well with a carrier fluid.

[0015] The coating may be applied to a portion of the metallic spheres or to the entire circumference of the spheres. The coating may function as a sealant to prevent invasion of the carrier fluid (as well other fluids in the wellbore) into the core. The coating may further provide greater anti-corrosive characteristics to the well treating composite.

[0016] Suitable coatings include phenolic resins, phenol-formaldehyde resins, melamine-formaldehyde resins, polyurethanes, carbamate resins, epoxy resins, polyamides, polyolefins, such as polyethylene, polystyrene and a combination thereof. In a preferred embodiment, the coating is an epoxy resin, phenol formaldehyde resin or a urethane resin.

[0017] The apparent specific gravity (ASG) of the hollow non-porous metallic spheres is generally less than or equal to 4.0, preferably less than or equal to 3.0. When employed in deep water environments having high closure stresses, such as when used as proppants, the spheres have a thicker wall and are characterized by an ASG which is preferably in the vicinity of from about 2.5 to about 4.0. The ASG of the spheres, when less harsh environments are encountered, is generally less than or equal to 2.0, generally between from about 1.05 to about 2.0.

[0018] The well treating agent and composite defined herein exhibit high compressive strength. Fracturing may therefore be conducted at closure stresses greater than about 500 psi and at temperatures ranging from ambient to 500° F. For example, spheres of a 1 mm diameter and an ASG of about 1.3 are capable of withstanding up to 20,000 psi. The high compressive strength exhibited by the spheres may be attributable to the stiffness of the metal. The high compressive strength may further be attributable to the cylindrical shape of the spheres upon them being subjected to high pressures. As high pressure is applied, such as by a mechanical press, the metallic spheres start to deform between the two platens and the two points of contact begin to cave. As the area exposed to the load increases, the deformed particulates resemble oriented cylinders. Such cylinders, along with their short length, offer tremendous strength to the particulates.

[0019] While the well treating agent and composite may be combined with fibrous reinforcing agents, typically the addition of fibrous reinforcing agents is unnecessary. The compressive strength of the well treating agent free of fibrous reinforcing agents is typically greater than the compressive strength of an aggregate composed of the same hollow non-porous metallic spheres and fibrous reinforcing agent.

[0020] A further benefit of the well treating agents of the invention is their ability to capture and trap spalding fines formed during closure. Such fines may be trapped within the deforming region of the spheres.

[0021] The well treating agent and composite of the invention finds particular applicability as proppants in the fracturing of hydrocarbon-bearing formations. In particular, the well treating agent or composite may be introduced into the well at concentrations sufficient to achieve a partial monolayer of proppant in the fracture.

[0022] The well treating agents of the invention, as well as composites comprising such well treating agents, may further be used in sand control. In such applications, the hollow non-porous metallic spheres (or composites) are typically introduced into the wellbore in a slurry of the carrier fluid. At least a portion of the well treating agent (or composite) is placed adjacent the subterranean formation to form a fluid-permeable pack. The pack is capable of reducing or substantially preventing the passage of formation particles from the subterranean formation into the wellbore. At the same time, formation fluids from the subterranean formation are permitted to pass into the wellbore.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] In order to more fully understand the drawings referred to in the detailed description of the present invention, a brief description of each drawing is presented, in which:

[0024] FIG. **1** is a schematic diagram of a particle compression cell used to test deformation of a metallic sphere of the invention.

[0025] FIG. **2** is a displacement-load curve for different metallic spheres defined by the invention.

[0026] FIG. **3** is a photograph of metallic spheres within the invention at the point of collapse at varying loads.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027] The well treating agent of the invention contains particulates of hollow metallic spheres. The metallic spheres may exhibit a minimal level of porosity, i.e., that level of porosity which is necessary for the release of internal gases from the spheres upon exposure of the spheres to elevated temperatures and/or pressures. Well treating agents exhibiting such minimal levels of porosity are hereinafter referred to as being “substantially non-porous”. Typically, the amount of porosity in such substantially non-porous metallic spheres is less than or equal to 1 volume percent based on the total volume of the metal which constitutes the metallic sphere. Alternatively, the hollow metallic spheres may be completely non-porous. (The reference herein to “hollow non-porous metallic spheres” shall refer to both those hollow metallic spheres which are completely non-porous as well as those metallic spheres which are substantially non-porous.)

[0028] The well treating agent may consist entirely of the hollow non-porous metallic spheres.

[0029] The hollow non-porous metallic spheres are typically lightweight and exhibit high strength. As such, they find particular applicability as proppant and sand control particulates in gravel packing and hydraulic fracturing. Preferably, such particulates have a sphericity of about 0.9, API RP 58, an important parameter for gravel packing as higher sphericity equates to relatively high permeability.

[0030] The particle size of the metallic spheres may be selected based on anticipated downhole conditions including the width of the anticipated fracture. Typically, the diameter of the spheres is in a range from about 4 mesh to about 100 mesh, alternatively from about 10 mesh to about 40 mesh. The spheres deform with stress and yet are sufficiently strong to be used on their own at high pressures, such as a closure stress in excess of 4,000 psi, when the spheres are used in a partial monolayer hydraulic fracturing application. The spheres are further capable of preventing sand grains and/or other formation fines from migrating into the wellbore in sand control applications.

[0031] The metallic spheres are made from conductive metal or alloy powders which, preferably, exhibit at least some resistance to corrosion at downhole fluids and downhole conditions. Such conductive metals may be stainless steel, iron, copper, nickel, cobalt, chromium, aluminum, molybdneum, titanium, silver, gold, tin, lead, steel, cast iron, brass, bronze, nickel alloys or a mixture or alloys thereof. Stainless steel alloy or carbon steel are preferred, as well as metals, such as iron, chromium, titanium, nickel, aluminum, cobalt or molybdenum or an alloy mixture of such metals. Stainless steel and titanium are most preferred.

[0032] The hollow metallic spheres may be produced by procedures known in the art. One such method is an electromagnetic levitation melting technique, disclosed in U.S. Pat. No. 4,565,571. In this process, a particulate material containing a conductive metal or alloy powder is formed which exhibits sufficient green strength to be substantially self-supporting. The green porous article is then subjected to an electromagnetic field which (i) has a field strength and frequency sufficient to exert a force in a direction such that the force of gravity acting on the green article is counterbalanced thereby levitating it in space, and (ii) has a frequency sufficient to induce an eddy current in the article of such intensity that the dissipation thereof produces sufficient heat to melt the electrically conductive metal. Pores are therefore entrapped in the pores of the green particle as well as any gases contained therein. The molten particle containing the entrapped pores may be heated for a longer period of time to expand the gases contained in the pores to a volume such that substantially all of the entrapped pores combine to produce a hollow molten metal sphere. The spheres are then cooled at a rate sufficient to solidify the molten metal.

[0033] Another method of manufacturing the hollow non-porous metallic spheres is by the continuous extrusion of a dispersion containing the particulate metal from a coaxial blowing nozzle, as disclosed in U.S. Pat. No. 4,867,931. This process uses an aqueous or volatile solvent containing dispersed metal oxide(s) which is capable of forming a film. The particle film may consist of a selection of metal oxides, such as iron oxide, nickel oxide, molybdeum oxide, chromium oxide, cobalt oxide and titanium hydride, mixed at the requisites percentages to yield the final desired alloy. The dispersion may also contain a binder, such as cellulose acetate or polyvinyl alcohol; a film stabilizing agent which may include an anionic surfactant, such as a salt of lauryl sulfate; and a dispersing agent which may include a sodium alkyl or sodium aryl sulfate. The dispersed phase is fed to a concentric, coaxial blowing nozzle, such that the inner nozzle supplies a blowing gas contacting the dispersing phase residing in the annulus near the orifice of the blowing nozzle. The blowing gas (typically nitrogen, argon or hydrogen) pushes through a thin layer of dispersing phase at the orifice creating a droplet or hollow sphere of dispersed phase. While falling, the droplet is heated to form a workable "green" hollow sphere of the oxide. The spheres are then gathered and heated in a kiln to a temperature between from about 400° C. to about and 800° C. in a reducing atmosphere of hydrogen. Heating in hydrogen reduces the oxides to the metal and water. The metallic spheres are then heated to a temperature between from about 1000° C. to about 1500° C. to strengthen the spheres in a sintering process. This process produces uniformly sized, hollow non-porous metallic spheres having a uniform wall thickness.

[0034] A coating is preferably applied to the circumference of the spheres to form a coated composite. While the coating may function as a sealant to prevent entry of the carrier fluid or other wellbore fluids into the core of the spheres, the non-porous nature of the metallic spheres typically often renders such a sealant unnecessary. The amount of coating, when present, is typically from about 0.5 to about 10% by weight of the composite.

[0035] The coating may be applied to the non-porous metallic spheres using any suitable method known in the art. For example, the process, as disclosed in U.S. Pat. No. 7,135,231, may consist of heating the metallic spheres to a temperature between from about 93° C. to about 425° C., adding the heated spheres to a mixing apparatus, if necessary, and then applying a coupling agent, such as a polyamine, onto the surface of the spheres. A resin coating may then be sputtered onto at least a portion of the surface of the spheres. If additional protection is necessary, the process can include sputtering additional resin coats onto the spheres in an incremental manner, such that the resultant coated sphere has a plurality of interleaved resin coats fully coating the spheres.

[0036] The coating of the composite may further function to counteract caustic downhole conditions on the metal of the spheres and thus may provide greater anti-corrosive characteristics to the well treating agent.

[0037] In another embodiment, the metallic spheres may be heated to a temperature between from about 93° C. to about 425° C. and a resinous coating then applied while the metallic spheres are being cooled.

[0038] Representative coatings for the composite include phenolic resins, phenol-formaldehyde resins, melamine-formaldehyde resins, polyurethanes, carbamate resins, epoxy resins, polyamides, polyolefins, such as polyethylene, polystyrene and a combination thereof. In a preferred embodiment, the coating is an epoxy resin, phenol formaldehyde resin or a urethane resin.

[0039] The apparent specific gravity (ASG) of the hollow non-porous metallic spheres is generally less than or equal to 4.0, preferably less than or equal to 3.0. The non-porous nature of the metallic spheres assists in keeping the ASG of the spheres to remain constant during transport.

[0040] When the well treating agents (or composites) are employed in deep water environments having high closure stresses, the ASG of the hollow non-porous metallic spheres is preferably between from about 2.5 to about 4.0. In such applications, fracturing may be conducted at closure stresses greater than about 1500 psi and at temperatures ranges between ambient and 260° C. As a result, the well treating agents defined herein, as well as composites containing the same, function well in ultra deep, hot, high closure stress applications.

[0041] For use in less harsh environments, the ASG of the hollow non-porous metallic spheres is generally less than or equal to 2.0, generally less than 1.5, more generally between from about 1.05 to about 2.0.

[0042] The spheres, either by themselves as well treating gent or as a composite, are generally introduced into the well with a carrier fluid. Any carrier fluid suitable for transporting the spheres into the well and/or subterranean formation fracture in communication therewith may be employed including, but not limited to, carrier fluids including a brine, salt water, unviscosified water, fresh water, potassium chloride solution, a saturated sodium chloride solution, liquid hydrocarbons, and/or a gas such as nitrogen or carbon dioxide. In a preferred embodiment, the carrier fluid is unviscosified water or brine.

[0043] The carrier fluid may be gelled, non-gelled or have a reduced or lighter gelling requirement. The latter may be referred to as "weakly gelled", i.e., having minimum sufficient polymer, thickening agent, such as a viscosifier, or friction reducer to achieve friction reduction when pumped downhole (e.g., when pumped down tubing, work string, casing, coiled tubing, drill pipe, etc.), and/or may be characterized as having a polymer or viscosifier concentration of from greater than 0 pounds of polymer per thousand gallons of base fluid to about 10 pounds of polymer per thousand gallons of base fluid, and/or as having a viscosity of from about 1 to about 10 centipoises. The non-gelled carrier fluid typically contains no polymer or viscosifer.

[0044] The use of a non-gelled carrier fluid eliminates a source of potential packing and/or formation damage and enhancement in the productivity of the well. Elimination of the need to formulate a complex suspension gel may further mean a reduction in tubing friction pressures, particularly in coiled tubing and in the amount of on-location mixing equipment and/or mixing time requirements, as well as reduced costs. In one embodiment employing a substantially neutrally buoyant particulate and a brine carrier fluid, mixing equipment need only include such equipment that is capable of (a) mixing the brine (dissolving soluble salts), and (b) homogeneously dispersing in the substantially neutrally buoyant particulate.

[0045] The carrier fluid may further contain one or more conventional additives to the well service industry such as a gelling agent, crosslinking agent, gel breaker, surfactant, biocide, surface tension reducing agent, foaming agent, defoaming agent, demulsifier, non-emulsifier, scale inhibitor, gas hydrate inhibitor, polymer specific enzyme breaker, oxidative breaker, buffer, clay stabilizer, paraffin inhibitor, anti-corrosion agent, acid, buffer, solvent or a mixture thereof and other well treatment additives known in the art. The addition of such additives to the carrier fluids minimizes the need for additional pumps required to add such materials on the fly.

[0046] The hollow non-porous metallic spheres (or composites containing the spheres) may be advantageously pre-suspended as a substantially neutrally buoyant particulate and stored in the carrier fluid (e.g., brine of near or substantially equal density), and then pumped or placed downhole as is, or diluted on the fly. The term "substantially neutrally buoyant" refers to hollow non-porous metallic spheres (or composites) that have an ASG sufficiently close to the ASG of the selected ungelled or weakly gelled carrier fluid (e.g., ungelled or weakly gelled completion brine, other aqueous-based fluid, slick water, or other suitable fluid) which allows pumping and satisfactory placement of the proppant/particulate using the selected ungelled or weakly gelled carrier fluid.

[0047] The well treating agents of the invention find particular applicability in the fracturing of hydrocarbon-bearing formations or water injection wells. While the hollow non-porous metallic spheres are ideally suited for use as proppants in partial monolayers, they are further useful in normal fracture packs and sand control packs. In a preferred embodiment of the invention, however, the well treating agents are used, in light of the lightweight and high strength of the hollow non-porous metallic spheres, in a fracturing fluid at concentrations sufficient to achieve a partial monolayer fracture. Since the hollow non-porous metallic spheres may be made in a variety of ASGs, when used in a dense, non-viscous brine, some particles may float; some settle and some remain buoyant for good distribution across the entire fracture height for uniform coverage of the fracture area. Thus, the hollow non-porous metallic spheres offer all the advantages of lightweight proppants without sacrificing strength. In addition, when the spheres fail to crush, they do not produce fines like ceramic and quartz based proppants.

[0048] The wall of the hollow non-porous metallic spheres of the well treating fluid are typically 100% metal and do not contain reinforcing agents. The compressive strength of the well treating agent free of fibrous reinforcing agents is typically greater than the compressive strength of a well treating agent composed of the same hollow non-porous metallic spheres and a fibrous reinforcing agent. Fibrous reinforcing agents, when used with metallic spheres, typically promote interconnecting voids in the spheres. See, for instance, U.S. Pat. No. 4,867,931. This, in turn, causes the metal spheres to fill with fluid. When used as well treating agents, the entry of fluids into the metal spheres would increase the ASG of the well treating agent when it is exposed to hydrostatic pressure. This, in turn, jeopardizes the placement of the spheres in a partial monolayer since heavier proppant falls faster upon entering the fracture due to gravitational affects. The non-porous metallic spheres (as well as composites containing the spheres) of the invention are capable of achieving a partial monolayer fracture since the proppant may be uniformly dispersed in the fracture at the time of closure.

[0049] In another preferred embodiment, the hollow non-porous metallic spheres and/or substantially neutrally buoyant metallic spheres (as well as composites containing such spheres) are used in a sand control method. The spheres (or composites) may be introduced into the wellbore in a slurry with the carrier fluid. The spheres (or composites) are placed adjacent the subterranean formation to form a fluid-permeable pack. The fluid permeable pack is capable of reducing or substantially preventing the passage of formation particles from the subterranean formation into the wellbore while at the same time allowing passage of formation fluids from the subterranean formation into the wellbore.

[0050] In a preferred gravel pack operation, a screen assembly may be placed or otherwise disposed within the wellbore so that at least a portion of the screen assembly is disposed adjacent the subterranean formation. (The gravel pack operation may further proceed using a screenless pack.) A slurry containing the hollow non-porous metallic spheres (or composites) may then be introduced into the wellbore and placed adjacent the subterranean formation by circulation or other suitable method. A fluid-permeable pack is formed in the annular area between the exterior of the screen and the interior of the wellbore which is capable of reducing or substantially preventing the passage of formation particles from the subterranean formation into the wellbore during production of fluids from the formation. At the same time, the permeable pack allows the passage of formation fluids from the subterranean formation through the screen into the wellbore. When the flow is reversed, the consolidated hollow metallic spheres will flow back (or composites) with minimal formation sands. Particularly advantageous results are obtained in horizontal gravel packing which are large, such as those 6,000 ft long.

[0051] The hollow non-porous metallic spheres (or composites containing the spheres) may be mixed with the carrier fluid in any manner suitable for delivering the mixture to a wellbore and/or subterranean formation. In one embodiment, the spheres (or composites) may be injected into a subterranean formation in conjunction with a hydraulic fracturing treatment or other treatment at pressures sufficiently high enough to cause the formation or enlargement of fractures, or to otherwise expose the particles to formation closure stress. Such other treatments may be near wellbore in nature (affecting near wellbore regions) and may be directed toward improving wellbore productivity and/or controlling the production of fracture proppant or formation sand.

[0052] The hollow non-porous metallic spheres (or composites containing the spheres) are further employed in frac-pack operations, especially in unconsolidated and semi-consolidated formations in order to facilitate fluid recovery while preventing particulate migration. The frac-pack operation typically embodies the features of both a fracturing operation and a gravel packing operation. The unconsolidated formation may initially be fractured using the particulate materials. Additional proppant may then be held in place in the wellbore by (a) packing the material around a gravel packing screen and/or (b) consolidating the proppant material by means of a resin coating.

[0053] The well treating agents of the invention are further highly effective in capturing and trapping fines formed from "spalling" which is caused by embedment of the hydraulic fracture proppant into the exposed faces of the rock during closure. Such fines may severely reduce fracture conductivity. Such fines may be trapped within the deforming region of the spheres and, as such, are prevented from entering into the proppant pack.

[0054] In other fracturing application that employ multi-layer proppant packs, the hollow non-porous metallic spheres (as well as composites containing such spheres) may also be added to conventional proppants in concentrations from 0.5% to 20%, based on the total weight of proppant, to minimize or prevent proppant from being dislodged from the sand pack. Proppant flowback occurs from high velocity fluids, such as treatment fluids, as formation fluids, such as oil or gas, pass through a multi-layer proppant pack. The ability of the hollow non-porous metal spheres to deform allows conventional proppants, under closure stresses in excess of 500 psi, to indent the surface of the hollow non-porous metallic spheres or composites. Because the concentration of hollow non-porous metallic spheres (or composites) are considerably less than the conventional proppant, the probability is high that multiple proppant grains will indent the surface of the hollow non-porous metallic spheres simultaneously. This indentation feature has shown considerable improvement in minimizing proppant flowback as discussed in U.S. Pat. No. 6,059,034.

EXAMPLES

[0055] The following examples will illustrate the practice of the present invention in preferred embodiments. Other embodiments within the scope of the claims herein will be apparent to one skilled in the art from consideration of the specification and practice of the invention as disclosed herein. It is intended that the specification, together with the example, be considered exemplary only, with the scope and spirit of the invention being indicated by the claims which follow.

[0056] Strength and stiffness are the basic physical properties that are measured to evaluate the effectiveness and deformation characteristics of hollow non-porous metallic spheres. The following test procedures were used to measure the deformation versus applied load for single metallic spheres. All the tests were conducted at 22° C.

[0057] The test cell, as shown in FIG. **1**, consisted of a cylindrical stainless steel base-pedestal and a movable steel piston. A single particulate of a hollow non-porous metallic sphere of maraging 200 steel was placed at the center of the pedestal surface. (Ten different spheres of maraging 200 steel were tested varying slightly in size and wall thickness.) The piston was placed over and in contact with the sphere. The hollow cylinder kept the piston in vertical alignment. The diameter of the pedestal and piston was one-inch.

[0058] The initial width of the sphere was determined by measuring the change in height of the movable piston after insertion of the proppant grain into the cell.

[0059] The test cell was placed in a United Calibration Corporation SSTM-5 mechanical press. Two linear variable differential transformers (LVDTs) were placed in parallel with the test cell and the change in position of the piston was measured as load was applied. The test was conducted at a constant load rate of 5 lbs/minute and the load (force) and particle displacement was recorded simultaneously as a function of time. The test was terminated at predetermined degrees of sphere deformation. The net displacement of the collapsing sphere was calculated by subtracting the test apparatus compliance from the gross displacement. (Test apparatus compliance was measured independently without a sphere in the cell). The strain in the direction of load was then calculated by dividing the initial width of the sphere into the net displacement.

[0060] FIG. **2** is a plot of force versus displacement of the data obtained and shows where the metallic spheres first began to deform. The average slope of the load-displacement curve provides a measure of stiffness of the metallic sphere. In all cases, the load-displacement curve displayed a positive slope due to the deformation of the metallic sphere that was in direct contact with the piston and pedestal. The differences in results are attributable to the slight variation in size and wall thickness of the spheres.

[0061] FIG. **3** pictures a collection of metallic spheres at varying stages of their collapse. The load at the point of deformation is also shown.

[0062] From the foregoing, it will be observed that numerous variations and modifications may be effected without departing from the true spirit and scope of the novel concepts of the invention.

What is claimed is:

1. A well treating agent comprising particulates consisting of hollow non-porous metallic spheres.

2. The well treating agent of claim **1**, wherein the metal is stainless steel alloy, carbon steel or a metal selected from the group consisting of iron, chromium, titanium, nickel, cobalt or molybdenum or an alloy mixture thereof.

3. The well treating agent of claim **2**, wherein the metal is stainless steel or titanium.

4. The well treating agent of claim **1**, further comprising a coating on at least a portion of the hollow non-porous metallic spheres.

5. The well treating agent of claim **4**, wherein the coating is selected from the group consisting of a phenolic resin, phenol-formaldehyde resin, melamine-formaldehyde resin, polyurethane, carbamate resin, epoxy resin, polyamide, polyethylene, polystyrene and a combination thereof.

6. The well treating agent of claim **5**, wherein the coating is selected from the group consisting of an epoxy resin, phenol formaldehyde resin and a urethane resin.

7. The well treating agent of claim **1**, wherein the apparent specific gravity of the core of the well treating agent is less than or equal to 4.0.

8. The well treating agent of claim **7**, wherein the apparent specific gravity of the core of the well treating agent is less than or equal to 3.0.

9. The well treating agent of claim **8**, wherein the apparent specific gravity of the core of the well treating agent is less than or equal to 2.0.

10. The well treating agent of claim **9**, wherein the apparent specific gravity of the core of the well treating agent is less than or equal to 1.5.

11. The well treating agent of claim **1**, wherein the apparent specific gravity of the core of the well treating agent is between from about 1.05 to about 2.0.

12. A proppant or sand control particulate composed of the well treating agent of claim **1**.

13. A method of treating a well which comprises introducing into the well a composition comprising the well treating agent of claim **1**.

14. The method of claim **13**, wherein the well treating agent is introduced into the well as part of a sand control and/or hydraulic fracturing operation.

15. The method of claim **13**, wherein the well treating agent is introduced into the well at concentrations sufficient to achieve a partial monolayer fracture.

16. The method of claim **14**, wherein the fracturing is conducted at a closure stress greater than about 1500 psi at a temperature greater than 150° F.

17. The method of claim **13**, wherein the apparent specific gravity of the well treating agent is less than or equal to 4.0.

18. The method of claim **17**, wherein the apparent specific gravity of the well treating agent is less than or equal to 3.0.

19. A well treating agent comprising a core and a coating on at least a portion of the core, wherein the core comprises hollow non-porous metallic spheres.

20. The well treating agent of claim **19**, wherein the coating is selected from the group consisting of a phenolic resin, phenol-formaldehyde resin, melamine-formaldehyde resin, polyurethane, carbamate resin, epoxy resin, polyamide, polyethylene, polystyrene and a combination thereof.

21. The well treating agent of claim **19**, wherein the coating is selected from the group consisting of an epoxy resin, phenol formaldehyde resin and a urethane resin.

22. The well treating agent of claim **19**, wherein the metal is stainless steel alloy, carbon steel or a metal selected from the group consisting of iron, chromium, titanium, nickel, cobalt or molybdenum or an alloy mixture thereof.

23. The well treating agent of claim **19**, wherein the apparent specific gravity of the well treating agent is less than or equal to 2.0.

24. The well treating agent of claim **23**, wherein the apparent specific gravity of the well treating agent is less than or equal to 1.5.

25. A proppant or sand control particulate composed of the well treating agent of claim **19**.

26. A method of treating a well which comprises introducing into the well a composition comprising the well treating agent of claim **19**.

27. The method of claim **26**, wherein the well treating agent is introduced into the well as part of a sand control and/or hydraulic fracturing operation.

28. The method of claim **27**, wherein the well treating agent is introduced into the well at concentrations sufficient to achieve a partial monolayer fracture.

29. The method of claim **27**, wherein the fracturing is conducted at a closure stress greater than about 1500 psi at a temperature greater than 150° F.

30. The method of claim **26**, wherein the apparent specific gravity of the well treating agent is less than or equal to 4.0.

31. The method of claim **30**, wherein the apparent specific gravity of the well treating agent is less than or equal to 3.0.

32. A well treating agent comprising a core of hollow non-porous metallic spheres, the core being free of a fibrous reinforcing agent, wherein the compressive strength of the well treating agent is greater than the compressive strength of a similar well treating agent containing a core of hollow non-porous metallic spheres and a fibrous reinforcing agent.

33. A sand control method for a wellbore penetrating a subterranean formation, comprising:

introducing into the wellbore a slurry comprising particulates and a carrier fluid, wherein the particulates are hollow non-porous metallic spheres;

placing at least a portion of the particulates adjacent the subterranean formation to form a fluid-permeable pack capable of reducing or substantially preventing the passage of formation particles from the subterranean formation into the wellbore while allowing passage of formation fluids from the subterranean formation into the wellbore.

34. The method of claim **33**, wherein the particulates have an apparent specific gravity less than or equal to 2.0.

35. The method of claim **33**, wherein the particulates have an apparent specific gravity between from about 1.05 to about 2.0.

* * * * *