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(54) Title: METHODS TO IMPROVE STABILITY OF HIGH SOLID CONTENT FLUID

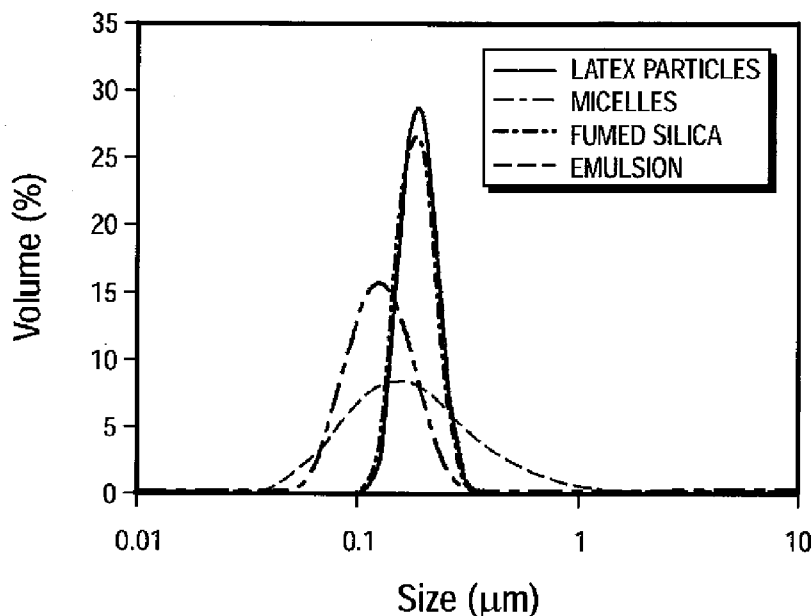


FIG. 1

(57) Abstract: A method of treating a subterranean formation of a well bore comprises providing a treatment fluid comprising a carrier fluid, a particulate material, a surfactant and micelles, wherein micelles are stabilized by the surfactant and act as particles in the treatment fluid; and introducing the treatment fluid into the wellbore.

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METHODS TO IMPROVE STABILITY OF HIGH SOLID CONTENT FLUID

Field of the Invention

[0001] The invention relates to methods for treating subterranean formations. More particularly, the invention relates to methods for improving the stability of high solid content fluid.

Background

[0002] The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

[0003] Hydrocarbons (oil, condensate, and gas) are typically produced from wells that are drilled into the formations containing them. For a variety of reasons, such as inherently low permeability of the reservoirs or damage to the formation caused by drilling and completion of the well, the flow of hydrocarbons into the well is undesirably low. In this case, the well is “stimulated” for example using hydraulic fracturing, chemical (usually acid) stimulation, or a combination of the two (called acid fracturing or fracture acidizing).

[0004] In hydraulic and acid fracturing, a first viscous fluid called the pad is typically injected into the formation to initiate and propagate the fracture. This is followed by a second fluid that contains a proppant to keep the fracture open after the pumping pressure is released. Granular proppant materials may include sand, ceramic beads, or other materials. In “acid” fracturing, the second fluid contains an acid or other chemical such as a chelating agent that can dissolve part of the rock, causing irregular etching of the fracture face and removal of some of the mineral matter, resulting in the fracture not completely closing when the pumping is stopped. Several types of viscosifiers are used to increase the viscosity of the fluid. These include polymers such as HEC, Xanthan, Guar etc and viscoelastic surfactants. Occasionally, hydraulic fracturing can be done without a

highly viscosified fluid (i.e., slick water) to minimize the damage caused by polymers or the cost of other viscosifiers.

[0005] In gravel packing, gravel is placed in the annulus of screen and formation/casing to control sand production. A carrier fluid is used to transport gravel from the surface to the formation where the gravel has to be placed. Typically two types of carrier fluids are used. The first is a brine with a low concentration of gravel (1lb per gal of brine) and the second is a viscous fluid with high concentration of gravel (5lb per gal of brine). Several types of viscosifiers are used to increase the viscosity of the fluid. These include polymers such as HEC, Xanthan, Guar etc and viscoelastic surfactants.

[0006] The transport of solids (proppant, gravel, or other particulate or solid material) from the surface to the required depth in the well plays an important role in well stimulations. A common problem that occurs during solids transport is the setting of solids due to difference in densities of the fluid and the solid particles. If the solids start settling before the fluid reaches its destination, several problems can occur including screen outs, incomplete gravel packs, wellbore blockage, stuck tools etc. To reduce the settling rate, the carrier fluid is typically viscosified using polymers or surfactants. However, increasing the viscosity of the fluid at the surface can increase the friction pressure significantly.

[0007] Methods disclosed herewith offer a new way to ensure the stability of the high solid content fluid while it is under downhole conditions.

Summary

[0008] According to some embodiments, the method comprises providing a treatment fluid comprising a carrier fluid, a particulate material, a surfactant and micelles, wherein micelles are stabilized by the surfactant and act as particles in the treatment fluid; and introducing the treatment fluid into the wellbore.

Brief Description of the Drawings

[0009] Figure 1 is a graph showing the particle size distributions of the submicron materials used in examples.

[00010] Figure 2 is a graph showing the leak-off results for examples.

Description

[00011] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementation—specific decisions must be made to achieve the developer's specific goals, such as compliance with system related and business related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time consuming but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure.

[00012] The description and examples are presented solely for the purpose of illustrating the preferred embodiments and should not be construed as a limitation to the scope. While the compositions are described herein as comprising certain materials, it should be understood that the composition could optionally comprise two or more chemically different materials. In addition, the composition can also comprise some components other than the ones already cited. In the summary and this detailed description, each numerical value should be read once as modified by the term "about" (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. Also, in the summary and this detailed description, it should be understood that a concentration range listed or described as being useful, suitable, or the like, is intended that any and every concentration within the range, including the end points, is to be considered as having been stated. For example, "a range of from 1 to 10" is to be read as indicating each and every possible number along the continuum between about 1 and about 10. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to only a

few specific, it is to be understood that inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that inventors possession of the entire range and all points within the range.

[00013] The following definitions are provided in order to aid those skilled in the art in understanding the detailed description.

[00014] The term “treatment”, or “treating”, refers to any subterranean operation that uses a fluid in conjunction with a desired function and/or for a desired purpose. The term “treatment”, or “treating”, does not imply any particular action by the fluid.

[00015] The term “fracturing” refers to the process and methods of breaking down a geological formation and creating a fracture, i.e. the rock formation around a well bore, by pumping fluid at very high pressures (pressure above the determined closure pressure of the formation), in order to increase production rates from a hydrocarbon reservoir. The fracturing methods otherwise use conventional techniques known in the art.

[00016] High solid content fluid (HSCF) shows promises in many aspects for fracturing fluid. For example, in shale gas formation, current practice requires high pumping rate with low viscosity fluid carrying low concentration of proppant to stimulate the formation. This brought obvious issues such as high water usage and high energy consumption. To make things worse, the effectiveness of the stimulation is not good since the fracture created this way cannot be properly propped and kept open for production. HSCF uses low water content, has high density and hence high hydrostatic pressure and low horse power requirement on treatments. In addition, the HSCF carries proppant wherever it fractured which ensures good stimulation efficiency.

[00017] For HSCF, fluid loss control is very important since small amount of fluid loss could render the fluid completely immobile. Fluid loss control for HSCF is achieved mainly by two methods. The first is to construct the HSCF with solid particles following a certain particle size distribution, where the holes created by bigger particles are filled by smaller particles. It has been demonstrated that if the particles construction follows Apollonian packing parameters, good leak off control can be achieved. The second method is to use polymer latex material when enough pressure differential is applied and liquid

content is reduced, the latex will film and form an impermeable barrier. Method one and two are used mostly in combination in the HSCF system since the leakoff control requirement is much higher than for conventional fluids and both method are needed. The particle packing creates small enough holes for the latex particles to plug and building film on.

[00018] For apollonian packing of particles to stop fluid loss, the particle sizes need to extend to a few nanometer sizes when the gap or capillaries formed in these packing systems will become small enough that close to 10,000 psi capillary pressure is presence. This pressure can essentially stop any fluid loss. It is not easy to have an ideal gradient of particles to achieve this good a fluid loss control. When it comes to production, the small particles also will need to be cleaned up to give good permeability to the producing fluid. For the latex case, in fluid loss process, the latex is very effective in building an impermeable layer that prevents fluid from leaking off to the formation. Since the polymer latex is used above its glass transition temperature, it is usually pliable and can deform to seal small gaps without the need to be exact in particle sizes. However, when it comes to production, the impermeable layer is very damaging, i.e. the formation fluid will not be able to produce through this layer. It is very difficult to degrade current latex film to regain permeability.

[00019] In the current disclosed embodiments, a new method/material is disclosed for both fluid loss control and cleanup of a high solid content fluid system.

[00020] A method and material to control fluid loss in the hydraulic fracturing treatment is disclosed. The leakoff control is achieved by using surfactant to form micelles and these micelles act as small “particles” to plug pore throats. The pore throats can be created by either the formation rock or the HSCF particle packing. Oil can be used to control the “particle” (droplet, or oil inclusive micelles, i.e. emulsion droplets) size to give best performances. Surfactant molecule sizes can also be changed to give different “particle” sizes. The micelles and/or emulsion droplet can act as particles for filling the right size of pore throats for fluid loss control. The droplets can also have certain flexibility (pliability) to deform and seal non-exact size pore throats. This method can be used together with the HSCF system, but is not limited to this system.

[00021] In further embodiment, the surfactant micelles or emulsion droplets can be destroyed after the stimulation. The destruction can be coming from emulsion droplet increases by diffuse in more oil (such as from formation), or react with a de-emulsifier, or degrading the emulsifier surfactant.

[00022] As described, fluid loss control can be achieved by using particles (including fine emulsion droplets) to plug the pore throats, creating an impermeable film by using sheet like material or latex materials. In order to stop leakoff, the particle size must be properly selected to match the pore throats. Impermeable film created by latex, is difficult to be cleaned up after the treatment, therefore will impair production of the well.

[00023] In the current disclosed embodiments, “particles” formed by surfactant micelles or oil droplets (for water as continuous phase, if oil is the continuous phase, then the droplets can be water droplets) stabilized by surfactant are used as fluid control agent. The particles formed this way can be controlled by the specific surfactant used, amount of discontinuous phase etc. A wide spectrum of particle sizes can be achieved in this way. Since the particles formed here are based on self assembly with Van der Waals force, they are not completely rigid particles. Under certain pressure, the particles can actually deform to accommodate some shape changes. The particles formed in this way will help fluid loss control by both plugging the right pores throats and be pliable to seal not perfectly fit holes. In another word, it has the property of a latex filming and particle property. It can form “film-like” low permeability layer during stimulation treatments. On the other hand, the film formed by this way will not have the permanent properties like a latex film. It can be destroyed by many ways. Once the film property is removed, the permeability is regained.

[00024] A few example fluids were tested to demonstrate the properties of the micelle or surfactant stabilized oil emulsion approach. Conventional static fluid loss tests were used to measure the performances (leakoff control) of these fluids. All tests in the examples were performed at room temperature. A water saturated ceramic disks with 10 microns opening were used as the substrate. A filter paper with 10 micron opening was placed on the substrate and the fluid samples were placed on top of the filter paper. A 500

psi differential pressure was applied and the effluent was collected out of the fluid loss cell for a period of 30-60 min.

[00025] Table 1 gives the fluid formulations used in the examples. In these examples, mesh sizes for the three bigger particles are given by the mesh size. Calcium carbonate have a d50 within the range of 2.5 - 3 micron, latex has a d50 of 175nm, fumed silica have size a d50 of 170 nm, micelle solution has micelle sizes of d50 of 120 nm, and the oil in water emulsion has a size of emulsion droplets with d50 of 160nm. The traces of particle size distributions of the submicron materials are given in Figure 1.

Fluid components in g	Baseline	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
Crystalline silica 40/70 mesh	206.7	206.7	206.7	206.7	206.7	206.7	206.7
Crystalline silica 100 mesh	34.98	34.98	34.98	34.98	34.98	34.98	34.98
Crystalline silica 400 mesh	31.8	31.8	31.8	31.8	31.8	31.8	31.8
Calcium Carbonate 2 micron (SafeCarb 2)		45.53	45.53	45.53	45.53	45.53	45.53
Other liquid components	2.34	2.34	2.34	2.34	2.34	2.34	2.34
Water	77.86	77.86	38.92	0	0	0	0
Latex		0	39.71	0	0	0	0
Particles solution (Fumed silica Aerodisp W7520)		0	0	87.2	0	0	0
Micelles solution ¹		0	0	0	77.86	0	0
Emulsion ² (Oil in Water)		0	0	0	0	75.52	0
Broken emulsion		0	0	0	0	0	75.52

Table 1

(1) Solution made with Rhodafac at above CMC concentration in water

(2) Emulsion made with oil/water = 1/3 and 2% Rhodafac with ultrasonic mixing (Omni Ruptor 400) at 70% power energy, pulser 90% for 1 min and used as is.

[00026] The leakoff results for 30 min of all the samples were plotted in Figure 2.

[00027] Baseline fluid we used a tri-modal system. It consists of the three coarser particles in the formulation system. Apparently, the packing (or filter cake) formed by these solid will still have big voids and pore throats. As a result, the leakoff control cannot be good, as shown in the Figure 2, the fluid inside the fluid loss cell cannot last for a few minutes before it was completely depleted.

[00028] Compared to baseline, sample A has another solid, which is 2 micron in size. It can be seen from Figure 2 that the fluid loss for A is much less than baseline since the big pore throats are now blocked by the 2 micron particles. However, this leakoff is still very high.

[00029] Sample B included a latex of 180 nm particle size comparing to sample A. These latex particles serve two purposes: first as a small particle that further plug the small pore throats created in the sample filter cake. Second is to give the cake a filming ability, where the latex particles fused together to form a close to completely impermeable layer. The fluid loss results can be seen in Figure 2. It gives the lowest leakoff value among all the samples shown.

[00030] If the filming ability is removed, i.e. without latex but with a non-filming particles, such as in sample C. In sample C, the latex component is replaced with fumed silica sample of approximately the same size as that of the latex. One can see from Figure 2 that sample C's fluid loss is more than that of sample B, but way less than that of sample A. This validates the function of latex to be both particle contributor and filming contributor.

[00031] Sample D used the micelle "particles". It can be seen that the fluid loss performance is close to that of sample C. This indicates that the particles formed by the

surfactant micelles gives a stable “particle” size but is not pliable that filming like latex did not happen.

[00032] Sample E still used the micelles, however, oil is added in these micelles. These “particles” are now oil in water emulsion droplets. From the fluid loss result in Figure 2, one can see that sample E’s fluid loss is visibly better than that of sample D, where the micelle “particles” are rigid, and no deformation can happen to give more contributions to the leakoff control. It indicates that there is a good chance that we can push the performances of the emulsion to that of a latex particle.

[00033] One of the goals to switch from latex to micelle or emulsion “particle” approach is to allow the particles to degrade after the job and give good cleanup of the fracture. Sample F demonstrated this idea. In sample F, the emulsion used in sample E was broken and fluid loss is show to have almost moved back to that of sample A, without the emulsion. This validates that the cleanup by breaking the emulsion is achievable.

[00034] The treatment fluid includes a carrier fluid, a particulate material, a surfactant and micelles, wherein micelles are stabilized by the surfactant and improves the high solid content fluid performances.

[00035] According to one embodiment, the treatment fluid is used as a fracturing fluid. The carrier fluid includes any base fracturing fluid understood in the art. Some non-limiting examples of carrier fluids include hydratable gels (e.g. guar, poly-saccharides, xanthan, hydroxy-ethyl-cellulose, etc.), a cross-linked hydratable gel, a viscosified acid (e.g. gel-based), an emulsified acid (e.g. oil outer phase), an energized fluid (e.g. an N₂ or CO₂ based foam), and an oil-based fluid including a gelled, foamed, or otherwise viscosified oil. Additionally, the carrier fluid may be a brine, and/or may include a brine. He carrier fluid may be water, DI water, tap water, seawater, produced water or any type of water available in the field.

[00036] The treatment fluid may comprise further a viscosifying agent. The viscosifying agent may be any crosslinked polymers. The polymer viscosifier can be a metal-crosslinked polymer. Suitable polymers for making the metal-crosslinked polymer viscosifiers include, for example, polysaccharides such as substituted galactomannans,

such as guar gums, high-molecular weight polysaccharides composed of mannose and galactose sugars, or guar derivatives such as hydroxypropyl guar (HPG), carboxymethylhydroxypropyl guar (CMHPG) and carboxymethyl guar (CMG), hydrophobically modified guar, guar-containing compounds, and synthetic polymers. Crosslinking agents based on boron, titanium, zirconium or aluminum complexes are typically used to increase the effective molecular weight of the polymer and make them better suited for use in high-temperature wells.

[00037] Other suitable classes of polymers effective as viscosifying agent include polyvinyl polymers, polymethacrylamides, cellulose ethers, liginosulfonates, and ammonium, alkali metal, and alkaline earth salts thereof. More specific examples of other typical water soluble polymers are acrylic acid-acrylamide copolymers, acrylic acid-methacrylamide copolymers, polyacrylamides, partially hydrolyzed polyacrylamides, partially hydrolyzed polymethacrylamides, polyvinyl alcohol, polyalkyleneoxides, other galactomannans, heteropolysaccharides obtained by the fermentation of starch-derived sugar and ammonium and alkali metal salts thereof.

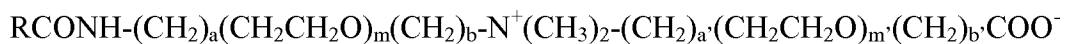
[00038] Cellulose derivatives are used to a smaller extent, such as hydroxyethylcellulose (HEC) or hydroxypropylcellulose (HPC), carboxymethylhydroxyethylcellulose (CMHEC) and carboxymethylcellulose (CMC), with or without crosslinkers. Xanthan, diutan, and scleroglucan, three biopolymers, have been shown to have excellent particulate-suspension ability even though they are more expensive than guar derivatives and therefore have been used less frequently, unless they can be used at lower concentrations.

[00039] In other embodiments, the viscosifying agent is made from a crosslinkable, hydratable polymer and a delayed crosslinking agent, wherein the crosslinking agent comprises a complex comprising a metal and a first ligand selected from the group consisting of amino acids, phosphono acids, and salts or derivatives thereof. Also the crosslinked polymer can be made from a polymer comprising pendant ionic moieties, a surfactant comprising oppositely charged moieties, a clay stabilizer, a borate source, and a metal crosslinker. Said embodiments are described in U.S. Patent Publications US2008-

0280790 and US2008-0280788 respectively, each of which are incorporated herein by reference.

[00040] The viscosifying agent may be a viscoelastic surfactant (VES). The VES may be selected from the group consisting of cationic, anionic, zwitterionic, amphoteric, nonionic and combinations thereof. Some non-limiting examples are those cited in U.S. Patents 6,435,277 (Qu et al.) and 6,703,352 (Dahayanake et al.), each of which are incorporated herein by reference. The viscoelastic surfactants, when used alone or in combination, are capable of forming micelles that form a structure in an aqueous environment that contribute to the increased viscosity of the fluid (also referred to as “viscosifying micelles”). These fluids are normally prepared by mixing in appropriate amounts of VES suitable to achieve the desired viscosity. The viscosity of VES fluids may be attributed to the three dimensional structure formed by the components in the fluids. When the concentration of surfactants in a viscoelastic fluid significantly exceeds a critical concentration, and in most cases in the presence of an electrolyte, surfactant molecules aggregate into species such as micelles, which can interact to form a network exhibiting viscous and elastic behavior.

[00041] In general, particularly suitable zwitterionic surfactants have the formula:



in which R is an alkyl group that contains from about 11 to about 23 carbon atoms which may be branched or straight chained and which may be saturated or unsaturated; a, b, a', and b' are each from 0 to 10 and m and m' are each from 0 to 13; a and b are each 1 or 2 if m is not 0 and (a + b) is from 2 to 10 if m is 0; a' and b' are each 1 or 2 when m' is not 0 and (a' + b') is from 1 to 5 if m is 0; (m + m') is from 0 to 14; and CH₂CH₂O may also be OCH₂CH₂. In some embodiments, a zwitterionic surfactants of the family of betaine is used.

[00042] Exemplary cationic viscoelastic surfactants include the amine salts and quaternary amine salts disclosed in U.S. Patent Nos. 5,979,557, and 6,435,277 which are

hereby incorporated by reference. Examples of suitable cationic viscoelastic surfactants include cationic surfactants having the structure:

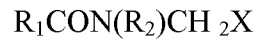


in which R_1 has from about 14 to about 26 carbon atoms and may be branched or straight chained, aromatic, saturated or unsaturated, and may contain a carbonyl, an amide, a retroamide, an imide, a urea, or an amine; R_2 , R_3 , and R_4 are each independently hydrogen or a C_1 to about C_6 aliphatic group which may be the same or different, branched or straight chained, saturated or unsaturated and one or more than one of which may be substituted with a group that renders the R_2 , R_3 , and R_4 group more hydrophilic; the R_2 , R_3 and R_4 groups may be incorporated into a heterocyclic 5- or 6-member ring structure which includes the nitrogen atom; the R_2 , R_3 and R_4 groups may be the same or different; R_1 , R_2 , R_3 and/or R_4 may contain one or more ethylene oxide and/or propylene oxide units; and X^- is an anion. Mixtures of such compounds are also suitable. As a further example, R_1 is from about 18 to about 22 carbon atoms and may contain a carbonyl, an amide, or an amine, and R_2 , R_3 , and R_4 are the same as one another and contain from 1 to about 3 carbon atoms.

[00043] Amphoteric viscoelastic surfactants are also suitable. Exemplary amphoteric viscoelastic surfactant systems include those described in U.S. Patent No. 6,703,352, for example amine oxides. Other exemplary viscoelastic surfactant systems include those described in U.S. Patents Nos. 6,239,183; 6,506,710; 7,060,661; 7,303,018; and 7,510,009 for example amidoamine oxides. These references are hereby incorporated in their entirety. Mixtures of zwitterionic surfactants and amphoteric surfactants are suitable. An example is a mixture of about 13% isopropanol, about 5% 1-butanol, about 15% ethylene glycol monobutyl ether, about 4% sodium chloride, about 30% water, about 30% cocoamidopropyl betaine, and about 2% cocoamidopropylamine oxide.

[00044] The viscoelastic surfactant system may also be based upon any suitable anionic surfactant. In some embodiments, the anionic surfactant is an alkyl sarcosinate. The alkyl sarcosinate can generally have any number of carbon atoms. Alkyl sarcosinates can have about 12 to about 24 carbon atoms. The alkyl sarcosinate can have about 14 to about 18 carbon atoms. Specific examples of the number of carbon atoms include 12, 14,

16, 18, 20, 22, and 24 carbon atoms. The anionic surfactant is represented by the chemical formula:



wherein R_1 is a hydrophobic chain having about 12 to about 24 carbon atoms, R_2 is hydrogen, methyl, ethyl, propyl, or butyl, and X is carboxyl or sulfonyl. The hydrophobic chain can be an alkyl group, an alkenyl group, an alkylarylalkyl group, or an alkoxyalkyl group. Specific examples of the hydrophobic chain include a tetradecyl group, a hexadecyl group, an octadecentyl group, an octadecyl group, and a docosenoic group.

[00045] The viscosifying agent may be present in lower amount than conventionally is included for a fracture treatment. The loading of a viscosifier, for example described in pounds of gel per 1,000 gallons of carrier fluid, is selected according to the particulate size (due to settling rate effects) and loading that the storable composition 106 must carry, according to the viscosity required to generate a desired fracture geometry, according to the pumping rate and casing or tubing configuration of the wellbore, according to the temperature of the formation of interest, and according to other factors understood in the art.

[00046] In certain embodiments, the low amount of a viscosifying agent includes a hydratable gelling agent in the carrier fluid at less than 20 pounds per 1,000 gallons of carrier fluid where the amount of particulates in the storable composition 106 are greater than 16 pounds per gallon of carrier fluid. In certain further embodiments, the low amount of a viscosifier includes a hydratable gelling agent in the carrier fluid at less than 20 pounds per 1,000 gallons of carrier fluid where the amount of particulates in the fracturing slurry 106 are greater than 23 pounds per gallon of carrier fluid. In certain embodiments, a low amount of a viscosifier includes a viscoelastic surfactant at a concentration below 1% by volume of carrier fluid. In certain embodiments, the low amount of a viscosifier includes the carrier fluid with no viscosifier included. In certain embodiments a low amount of a viscosifier includes values greater than the listed examples, because the circumstances of the storable composition conventionally utilize viscosifier amounts much greater than the examples. For example, in a high temperature application with a high proppant loading, the carrier fluid may conventionally indicate a viscosifier at 50 lbs. of

gelling agent per 1,000 gallons of carrier fluid, wherein 40 lbs. of gelling agent, for example, may be a low amount of viscosifier. One of skill in the art can perform routine tests of storable composition based on certain particulate blends in light of the disclosures herein to determine acceptable viscosifier amounts for a particular embodiment.

[00047] In certain embodiments, the carrier fluid includes an acid. The fracture may be a traditional hydraulic bi-wing fracture, but in certain embodiments may be an etched fracture and/or wormholes such as developed by an acid treatment. The carrier fluid may include hydrochloric acid, hydrofluoric acid, ammonium bifluoride, formic acid, acetic acid, lactic acid, glycolic acid, maleic acid, tartaric acid, sulfamic acid, malic acid, citric acid, methyl-sulfamic acid, chloro-acetic acid, an amino-poly-carboxylic acid, 3-hydroxypropionic acid, a poly-amino-poly-carboxylic acid, and/or a salt of any acid. In certain embodiments, the carrier fluid includes a poly-amino-poly-carboxylic acid, and is a trisodium hydroxyl-ethyl-ethylene-diamine triacetate, mono-ammonium salts of hydroxyl-ethyl-ethylene-diamine triacetate, and/or mono-sodium salts of hydroxyl-ethyl-ethylene-diamine tetra-acetate. The selection of any acid as a carrier fluid depends upon the purpose of the acid – for example formation etching, damage cleanup, removal of acid-reactive particles, etc., and further upon compatibility with the formation, compatibility with fluids in the formation, and compatibility with other components of the fracturing slurry and with spacer fluids or other fluids that may be present in the wellbore. The selection of an acid for the carrier fluid is understood in the art based upon the characteristics of particular embodiments and the disclosures herein.

[00048] The treatment fluid includes a particulate material. In one embodiment, the particulate material is a blend made of proppant. Proppant selection involves many compromises imposed by economical and practical considerations. Criteria for selecting the proppant type, size, size distribution in multimodal proppant selection, and concentration is based on the needed dimensionless conductivity, and can be selected by a skilled artisan. Such proppants can be natural or synthetic (including but not limited to glass beads, ceramic beads, sand, and bauxite), coated, or contain chemicals; more than one can be used sequentially or in mixtures of different sizes or different materials. The proppant may be resin coated (curable), or pre-cured resin coated. Proppants and gravels in the same or different wells or treatments can be the same material and/or the same size as

one another and the term proppant is intended to include gravel in this disclosure. In some embodiments, irregular shaped particles may be used. International application WO 2009/088317 discloses a method of fracturing with a slurry of proppant containing from 1 to 100 percent of stiff, low elasticity, low deformability elongated particles. US patent application 2007/768393 discloses proppant that is in the form of generally rigid, elastic plate-like particles having a maximum to minimum dimension ratio of more than about 5, the proppant being at least one of formed from a corrosion resistant material or having a corrosion resistant material formed thereon. In general the proppant used will have an average particle size of from about 0.15 mm to about 4.76 mm (about 100 to about 4 U. S. mesh), preferably from about 0.15 mm to about 3.36 mm (about 100 to about 6 U. S. mesh), more preferably from about 0.15 mm to about 4.76 mm (about 100 to about 4 U. S. mesh), more particularly, but not limited to 0.25 to 0.42 mm (40/60 mesh), 0.42 to 0.84 mm (20/40 mesh), 0.84 to 1.19 mm (16/20 mesh), 0.84 to 1.68 mm (12/20 mesh) and 0.84 to 2.38 mm (8/20 mesh) sized materials. Normally the proppant will be present in the slurry in a concentration from about 0.12 to about 0.96 kg/L, or from about 0.12 to about 0.72 kg/L, or from about 0.12 to about 0.54 kg/L. Also, there are slurries where the proppant is at a concentration up to 16 PPA (1.92 kg/L). If the slurry is foamed the proppant is at a concentration up to 20 PPA (2.4 kg/L). The storable composition is not a cement slurry composition.

[00049] The treatment fluid is a slurry comprising particulate materials with defined particles size distribution. One example of realization is disclosed in U.S. patent 7,784,541, herewith incorporated by reference in its entirety. In certain embodiments, the selection of the size for the first amount of particulates is dependent upon the characteristics of the propped fracture, for example the closure stress of the fracture, the desired conductivity, the size of fines or sand that may migrate from the formation, and other considerations understood in the art. In certain further embodiments, the selection of the size for the first amount of particulates is dependent upon the desired fluid loss characteristics of the first amount of particulates as a fluid loss agent, the size of pores in the formation, and/or the commercially available sizes of particulates of the type comprising the first amount of particulates.

[00050] In certain embodiments, the selection of the size of the second amount of particulates is dependent upon maximizing or optimizing a packed volume fraction (PVF) of the mixture of the first amount of particulates and the second amount of particulates. The packed volume fraction or packing volume fraction (PVF) is the fraction of solid content volume to the total volume content. A second average particle size of between about seven to ten times smaller than the first amount of particulates contributes to maximizing the PVF of the mixture, but a size between about three to twenty times smaller, and in certain embodiments between about three to fifteen times smaller, and in certain embodiments between about three to ten times smaller will provide a sufficient PVF for most slurry. Further, the selection of the size of the second amount of particulates is dependent upon the composition and commercial availability of particulates of the type comprising the second amount of particulates. In certain embodiments, the particulates combine to have a PVF above 0.70, 0.74 or 0.75 or above 0.80. In certain further embodiments the particulates may have a much higher PVF approaching 0.95. The optimization of the particles sizes distribution (Apollonian distribution), and dispersion of particles with high surface area lead to make fluids with high solid content (solid volume fraction from 50 to 70%).

[00051] The slurry may further include a third amount of particulates having a third average particle size that is smaller than the second average particle size. In certain further embodiments, the slurry may have a fourth, a fifth or a sixth amount of particles. Also in some embodiments, the same chemistry can be used for the third, fourth, fifth or sixth average particle size. Also in some embodiments, different chemistry can be used for the same third average particle size: e.g. in the third average particle size, half of the amount is a certain type of proppant and the other half is another type of proppant. For the purposes of enhancing the PVF of the slurry, more than three or four particles sizes will not typically be required. However, additional particles may be added for other reasons, such as the chemical composition of the additional particles, the ease of manufacturing certain materials into the same particles versus into separate particles, the commercial availability of particles having certain properties, and other reasons understood in the art.

[00052] The treatment fluid comprises fumed silica. Fumed silica also known as pyrogenic silica consists of microscopic droplets of amorphous silica fused into branched,

chainlike, three-dimensional secondary particles which then agglomerate into tertiary particles. The resulting powder has an extremely low bulk density and high surface area. The fumed silica is present in the treatment fluid in a concentration to reduce the settling rate of the particulate material in the treatment fluid. The concentration is less than about 2% by weight of the treatment fluid. In further embodiment, the concentration is less than about 1% by weight of the treatment fluid. In further embodiment, the concentration is less than about 0.6% by weight of the treatment fluid. In further embodiment, the concentration is in the range of about 0.001% to about 0.5% by weight of the treatment fluid. In further embodiment, the concentration is in the range of about 0.1% to about 0.5% by weight of the treatment fluid. Fumed silica particles are compatible with current common additives: leak-off control additives (latex, nanoparticles, viscosifier...) and antifoam, dispersant, surfactant.

[00053] According to a further embodiment, the treatment fluid further comprises a degradable material. In certain embodiments, the degradable material includes at least one of a lactide, a glycolide, an aliphatic polyester, a poly (lactide), a poly (glycolide), a poly (ϵ -caprolactone), a poly (orthoester), a poly (hydroxybutyrate), an aliphatic polycarbonate, a poly (phosphazene), and a poly (anhydride). In certain embodiments, the degradable material includes at least one of a poly (saccharide), dextran, cellulose, chitin, chitosan, a protein, a poly (amino acid), a poly (ethylene oxide), and a copolymer including poly (lactic acid) and poly (glycolic acid). In certain embodiments, the degradable material includes a copolymer including a first moiety which includes at least one functional group from a hydroxyl group, a carboxylic acid group, and a hydrocarboxylic acid group, the copolymer further including a second moiety comprising at least one of glycolic acid and lactic acid.

[00054] In an embodiment, the degradable material is selected from substituted and unsubstituted lactide, glycolide, polylactic acid, polyglycolic acid, copolymers of polylactic acid and polyglycolic acid, copolymers of glycolic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, copolymers of lactic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, and mixtures of such materials. Preferred examples are polyglycolic acid or PGA, and polylactic acid or PLA. These materials function as solid-acid precursors, and upon

dissolution in the fracture, can form acid species which can have secondary functions in the fracture as for example clean-up of the unwanted particulate material or treatment fluid additives.

[00055] In some embodiments, the treatment fluid can be made to be partially degradable when particles other than proppant are degradable i.e. they could disappear after a certain amount of time (following different processes: thermal degradation, thermal decomposition, dissolution etc.). Degradation of particles leads to increase the permeability of the proppant pack. Degradation should take place after placement. Several kind of degradable particles can be used, mineral (salt...) or organic (PLA, PGA, wax...) or any combination of them.

[00056] In some embodiments, the treatment fluid can comprise fiber. A first type of fiber additive can provide reinforcement and consolidation of the proppant. This fiber type can include, for example, glass, ceramics, carbon and carbon-based compounds, metals and metallic alloys, and the like and combinations thereof, as a material that is packed in the proppant to strengthen the proppant pillars. And in other applications, a second type of fiber can be used that inhibits settling of the proppant in the treatment fluid. The second fiber type can include, for example, polylactic acid, polyglycolic acid, polyethylterephthalate (PET), polyol, and the like and combinations thereof, as a material that inhibits settling or dispersion of the proppant in the treatment fluid and serves as a primary removable fill material in the spaces between the pillars. Yet other applications include a mixture of the first and second fiber types, the first fiber type providing reinforcement and consolidation of the proppant and the second fiber type inhibiting settling of the proppant in the treatment fluid.

[00057] The fibers can be hydrophilic or hydrophobic in nature. Hydrophilic fibers are preferred in one embodiment. Fibers can be any fibrous material, such as, but not necessarily limited to, natural organic fibers, comminuted plant materials, synthetic polymer fibers (by non-limiting example polyester, polyaramide, polyamide, novoloid or a novoloid-type polymer), fibrillated synthetic organic fibers, ceramic fibers, inorganic fibers, metal fibers, metal filaments, carbon fibers, glass fibers, ceramic fibers, natural polymer fibers, and any mixtures thereof. Particularly useful fibers are polyester fibers

coated to be highly hydrophilic, such as, but not limited to, DACRON® polyethylene terephthalate (PET) Fibers available from Invista Corp. Wichita, Kans., USA, 67220. Other examples of useful fibers include, but are not limited to, polylactic acid polyester fibers, polyglycolic acid polyester fibers, polyvinyl alcohol fibers, and the like.

[00058] In some embodiments, the treatment fluid may optionally further comprise additional additives, including, but not limited to, acids, fluid loss control additives, gas, corrosion inhibitors, scale inhibitors, catalysts, clay control agents, biocides, friction reducers, combinations thereof and the like. For example, in some embodiments, it may be desired to foam the first or second treatment fluid using a gas, such as air, nitrogen, or carbon dioxide.

[00059] The treatment fluids may be used for carrying out a variety of subterranean treatments, including, but not limited to, drilling operations, fracturing treatments, and completion operations (e.g., gravel packing). In some embodiments, the treatment fluids may be used in treating a portion of a subterranean formation. In certain embodiments, a treatment fluid may be introduced into a well bore that penetrates the subterranean formation. Optionally, the treatment fluid further may comprise particulates and other additives suitable for treating the subterranean formation. For example, the treatment fluid may be allowed to contact the subterranean formation for a period of time. In some embodiments, the treatment fluid may be allowed to contact hydrocarbons, formations fluids, and/or subsequently injected treatment fluids. After a chosen time, the treatment fluid may be recovered through the well bore. In certain embodiments, the treatment fluids may be used in fracturing treatments.

[00060] The method is also suitable for gravel packing, or for fracturing and gravel packing in one operation (called, for example frac and pack, frac-n-pack, frac-pack, StimPac treatments, or other names), which are also used extensively to stimulate the production of hydrocarbons, water and other fluids from subterranean formations. These operations involve pumping a slurry of in hydraulic fracturing or gravel in gravel packing. In low permeability formations, the goal of hydraulic fracturing is generally to form long, high surface area fractures that greatly increase the magnitude of the pathway of fluid flow from the formation to the wellbore. In high permeability formations, the goal of a

hydraulic fracturing treatment is typically to create a short, wide, highly conductive fracture, in order to bypass near-wellbore damage done in drilling and/or completion, to ensure good fluid communication between the rock and the wellbore and also to increase the surface area available for fluids to flow into the wellbore.

[00061] In certain embodiments, the treatment fluids may be used for providing some degree of sand control in a portion of the subterranean formation. In the sand control embodiments, the treatment fluid is introduced into the well bore that penetrates the subterranean formation such that the particulates form a gravel pack in or adjacent to a portion of the subterranean formation.

[00062] The foregoing disclosure and description of the invention is illustrative and explanatory thereof and it can be readily appreciated by those skilled in the art that various changes in the size, shape and materials, as well as in the details of the illustrated construction or combinations of the elements described herein can be made without departing from the spirit of the invention.

Claims

What is claimed is:

1. A method of treating a subterranean formation of a well bore, comprising:
 - a. providing a treatment fluid comprising a carrier fluid, a particulate material, a surfactant and micelles, wherein micelles are stabilized by the surfactant and act as particles in the treatment fluid; and
 - b. introducing the treatment fluid into the wellbore.
2. The method of claim 1, wherein the particulate material is proppant.
3. The method of claim 1, wherein the treatment fluid further comprises a viscosifying agent.
4. The method of claim 1, wherein the treatment fluid further comprises a degradable material.
5. The method of claim 4, wherein the particulate material has a first average particle size and the degradable particulate material has a second average particle size, wherein the second average particle size is between three to twenty times smaller than the first average particle size.
6. The method of claim 5, wherein the second average particle size is between five to ten times smaller than the first average particle size.
7. The method of claim 5, wherein the degradable particulate material has further an amount of particulates having a third average particle size, wherein the third average particle size is between three to twenty times smaller than the second average particle size.
8. A method of treating a subterranean formation of a well bore, comprising:
 - a. providing a treatment fluid comprising a carrier fluid, a particulate material,

a surfactant and micelles having an average size below 1 micron, wherein micelles are stabilized by the surfactant and act as particles in the treatment fluid; and

- b. introducing the treatment fluid into the wellbore.
9. The method of claim 8, wherein the micelles have an average size in the range of 10 nanometers to 500 nanometers.
 10. The method of claim 9, wherein the micelles have an average size in the range of 50 nanometers to 200 nanometers.
 11. The method of claim 9, wherein the particulate material is proppant.
 12. The method of claim 9, wherein the treatment fluid further comprises a viscosifying agent.
 13. The method of claim 9, wherein the treatment fluid further comprises a degradable material.
 14. The method of claim 13, wherein the particulate material has a first average particle size and the degradable particulate material has a second average particle size, wherein the second average particle size is between three to twenty times smaller than the first average particle size.
 15. The method of claim 14, wherein the second average particle size is between five to ten times smaller than the first average particle size.
 16. The method of claim 14, wherein the degradable particulate material has further an amount of particulates having a third average particle size, wherein the third average particle size is between three to twenty times smaller than the second average particle size.
 17. A method of fracturing a subterranean formation of a well bore, comprising:

- a. providing a treatment fluid comprising a carrier fluid, a particulate material, a surfactant and micelles having an average size below 1 micron, wherein micelles are stabilized by the surfactant and act as particles in the treatment fluid; and
 - b. introducing the treatment fluid into the wellbore to initiate or propagate a fracture.
18. The method of claim 17, wherein the micelles have an average size in the range of 10 nanometers to 500 nanometers.
19. The method of claim 18, wherein the micelles have an average size in the range of 50 nanometers to 200 nanometers.
20. The method of claim 17, wherein the particulate material is proppant.

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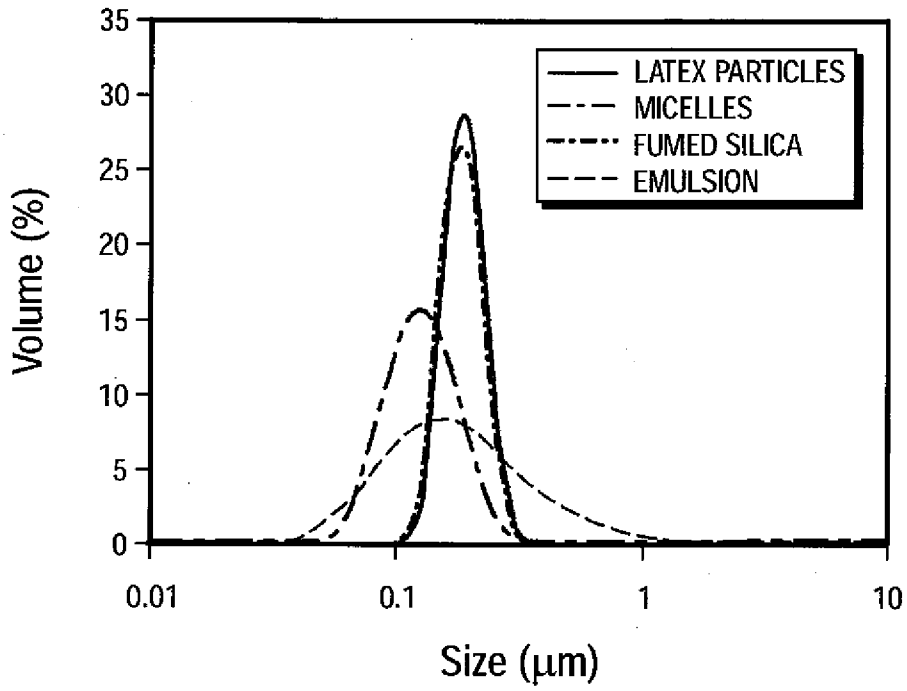


FIG. 1

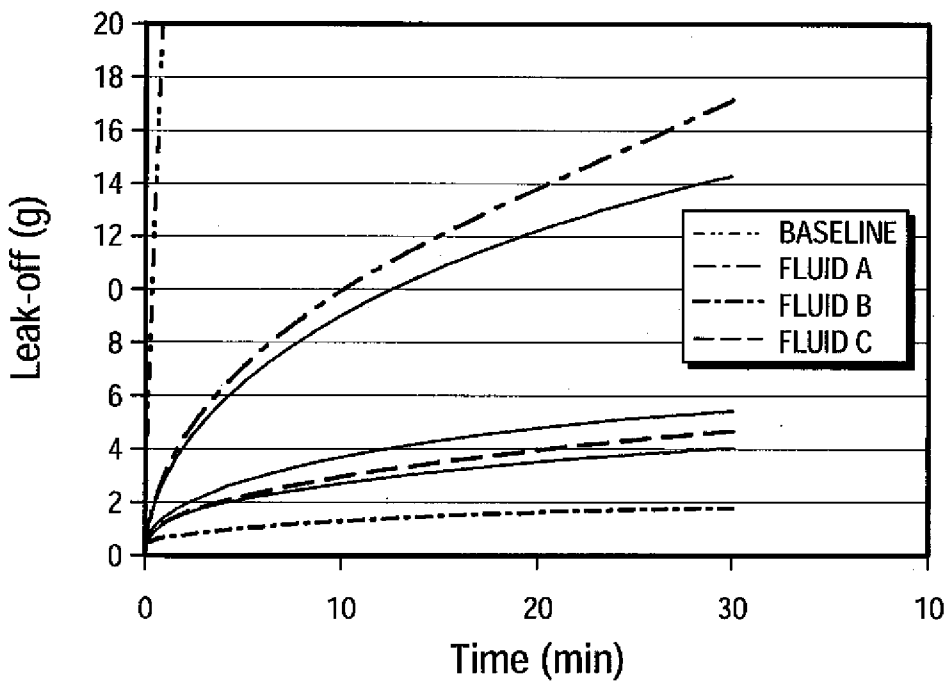


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No PCT/US2012/041097

A. CLASSIFICATION OF SUBJECT MATTER INV. C09K8/035 C09K8/50 C09K8/68 C09K8/575 ADD.				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) C09K				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 2011/071056 A1 (SAINI RAJESH K [US] ET AL) 24 March 2011 (2011-03-24) paragraphs [0036], [0037]; claims 8,11 the whole document -----	1-20		
X A	EP 0 835 983 A2 (SOFITECH NV [BE]; SCHLUMBERGER CIE DOWELL [FR] SOFITECH NV [BE]; DOWEL) 15 April 1998 (1998-04-15) page 5, line 50 - page 6, line 15; claims 1,2; figures 4-7 the whole document -----	1-3,8, 11,12, 17,20 4-7,9, 10, 13-16, 18,19		
X A	US 2009/209438 A1 (THIEME KARENA [CA] ET AL) 20 August 2009 (2009-08-20) claims 1-3,10 the whole document -----	1,2,8, 11,17,20 3-7,9, 10, 12-16, 18,19		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents : <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">7 September 2012</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">17/09/2012</div>		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">Straub, Thomas</div>		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2012/041097

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