



(43) International Publication Date
1 September 2016 (01.09.2016)

(10) International Publication Number
WO 2016/135253 A1

(51) International Patent Classification:
C09K 8/88 (2006.01) *E21B 43/267* (2006.01)

Tecnología Repsol, Carretera Extremadura (A-V), Km 18,
E-28935 Móstoles - Madrid (ES).

(21) International Application Number:
PCT/EP2016/054004

(74) Agent: **FERNÁNDEZ ARIZPE, Almudena**; ABG Pat-
entes, S.L., Avenida de Burgos, 16D, Edificio Euromor, E-
28036 Madrid (ES).

(22) International Filing Date:
25 February 2016 (25.02.2016)

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
15382079.0 26 February 2015 (26.02.2015) EP

(71) Applicant: **REPSOL, S.A.** [ES/ES]; Méndez Álvaro, 44,
E-28045 Madrid (ES).

(72) Inventors: **LÓPEZ REYES, Manuel**; Repsol, S.A.,
Centro de Tecnología Repsol, Carretera Extremadura (A-
V), Km 18, E-28935 Móstoles - Madrid (ES). **BEZERRA
DE MELO, Ricardo César**; Repsol, S.A., Centro de
Tecnología Repsol, Carretera Extremadura (A-V), Km 18,
E-28935 Móstoles - Madrid (ES). **CANAL VILA, Jacobo**;
Repsol, S.A., Centro de Tecnología Repsol, Carretera Ex-
tremadura (A-V), Km 18, E-28935 Móstoles - Madrid
(ES). **MARTÍNEZ CEBRIÁN, Itziar**; Repsol Explora-
ción, S.A., Campus Repsol, Méndez Álvaro, 44, E-28045
Madrid (ES). **LOLLEY BOWEN, Richard Llewellyn**;
Repsol Exploración, S.A., Campus Repsol, Méndez
Álvaro, 44, E-28045 Madrid (ES). **MONTENEGRO
GARCÍA, Ana Isabel**; Repsol Química, S.A., Centro de

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: ULTRA-HIGH-MOLECULAR-WEIGHT POLYOLEFIN PROPPANTS

(57) Abstract: The present invention relates to the use of ultra-high-molecular-weight polyolefin particles as proppants for treating subterranean formations, as well as to compositions comprising said particles and to fracturing methods employing said particles.



WO 2016/135253 A1

ULTRA-HIGH-MOLECULAR-WEIGHT POLYOLEFIN PROPPANTS

FIELD OF THE INVENTION

The present invention relates generally to proppants and their use in fracturing
5 operations for subterranean formations. More particularly, the present invention relates
to ultra-high-molecular-weight polyolefin proppants and their use in fracturing
operations for subterranean formations.

PRIOR ART

- 10 In oil and gas operations, stimulation or treatment of subterranean formations using a
fluid containing suspended particles may be used to improve production. This process is
generally known as hydraulic fracturing. In particular, a fluid, referred to in the art as a
treatment fluid, is usually pumped or injected through a wellbore into the subterranean
formation to be stimulated at a rate and pressure such that existing fractures are opened
15 and/or new fractures are formed and extended into the subterranean formation,
increasing the inflow area. The treatment fluid carries particles, referred to in the art as
proppant particles, into the fractures. The particles are placed in the fractures and the
fracturing fluid dissipates into the subterranean formation and/or is returned to the
surface. The particles function to "prop" open or prevent the fractures from totally
20 closing the formation fractured faces back together, whereby conductive channels
remain through which produced fluids can flow to the wellbore. Hydraulic fracturing is
particularly useful in stimulating the productivity of gas and oil wells in low
permeability reservoirs, but may also be applied to moderate to high permeability
reservoirs to overcome any potential damage the reservoir may have suffered.
- 25 The degree of success of a hydraulic fracturing operation depends greatly upon effective
fracture conductivity once the pumping of proppant laden fluid is finished and
production is begun. The conductivity of a fracture is largely given by the permeability
to extracted fluids of the proppant particles packed into the fracture times the average
effective fracture width, this must be higher than the reservoir capacity of delivering
30 fluids into the fracture. Proppant particulates should agglomerate within the fracture

- 2 -

such that they form interstitial spaces through which the fluid to be extracted can flow. Generally, the larger the interstitial spaces between proppant particles, the greater the permeability and hence conductivity of the fracture.

A crucial factor determining the permeability of proppant particles is their resistance to fracture closure stress. Resistance to fracture closure stress must be such that the proppant particles do not break into smaller fragments or fines which can reduce the permeability of the propped fracture by plugging it, resulting in a decreased productivity of fluid extraction from the well over time. Plugging may also occur when proppant particles deform in excess when subjected to fracture closure stress.

If the interstitial spaces of a propping particulate are too large, this may lead to reduced resistance to fracture closure. Therefore, the configuration of ideal propping particulates is one that is sufficiently porous so as to maximize the flow of extracted fluid, but not so porous so as to disintegrate or greatly deform under fracture closure stress.

Propping compositions are traditionally based on sand, glass or ceramics. However, these types of proppants generally tend to be relatively prone to disintegration or crushing into fines. Many efforts have therefore involved the careful study and modification of the different physical properties underlying the behavior of classical proppants. A particularly popular line of investigation has been the modification of classical proppants with polymeric resins, as disclosed for example in US 2007/0144736 A1.

Other efforts diverging more from classical proppant compositions introduce polymeric materials themselves as the constitutive component of proppant compositions. WO 2013/036350 A1 for instance describes methods for treating subterranean formations by injecting into the subterranean formation a fluid composition that includes a fluid and a deformable proppant having an interpenetrating polymer network formed from a first polymer component and a second polymer component. WO2013/068325 discloses proppant particulates comprising at least one aromatic polycondensation polymer having a glass transition temperature (T_g) of at least 120°C.

A group of polymers of particular relevance to the present invention are polyolefins. US2008/0060809 provides a method of fracturing a portion of a subterranean formation with a slurry comprising a fracturing fluid and high density plastic particulates among which polyolefins are considered together with an exhaustive list of other polymers. US

- 3 -

2009/0095473 A1 describes a method of fracturing a hydrocarbon-bearing formation which involves introducing into the formation a proppant comprising a composite of a porous polyolefin treated with a coating layer. US 2013/0092374 A1 discloses a proppant composition comprising a substantially deformable organic polymer which
5 may be high density polyethylene, polyethylene terephthalate or polypropylene.

A continuous need however exists to develop new proppant compositions which enrich the number of fracturing solutions available to the oil/gas industry.

SUMMARY OF THE INVENTION

10 The authors of the present invention have found that the use of particles of ultrahigh molecular weight polyolefin as proppants in fracturing processes confers many advantages over classical proppants or other polymers.

Thus, an aspect of the present invention relates to the use of particles comprising an ultra-high-molecular-weight polyolefin as proppants for treating a subterranean
15 formation, wherein the ultra-high-molecular-weight polyolefin has a viscosity average molecular weight ranging from 0.8×10^6 to 12×10^6 g/mol, an apparent density lying in the range from 0.2 to 0.7 g/mL, and wherein the sphericity of the particles is 0.5 or higher.

Another aspect of the invention refers to a fracturing composition comprising:

- 20 a) particles comprising an ultra-high-molecular-weight polyolefin, wherein the ultra-high-molecular-weight polyolefin has a viscosity average molecular weight ranging from 0.8×10^6 to 12×10^6 g/mol, and an apparent density lying in the range from 0.2 to 0.7 g/mL, and wherein the sphericity of the particles is 0.5 or higher, and
25 b) a treatment fluid suitable for carrying the particles.

In yet another aspect, the invention relates to a method of treating a subterranean geological formation penetrated by a wellbore, the method comprising injecting into the wellbore:

- 30 a) a plurality of particles, said particles comprising an ultra-high-molecular-weight polyolefin, wherein the ultra-high-molecular-weight polyolefin has a

- 4 -

viscosity average molecular weight ranging from 0.8×10^6 to 12×10^6 g/mol, an apparent density lying in the range from 0.2 to 0.7 g/mL, and wherein the sphericity of the particles is 0.5 or higher; or

b) a fracturing composition according to the invention.

5

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the use of particles comprising an ultra-high-molecular-weight polyolefin as proppants for treating a subterranean formation. Ultra-high molecular weight polyolefin is a general term commonly used to refer to
10 macromolecular polyolefins with molecular weights in the 10^6 g/mol range or higher. This term is however not intended to delimit the molecular weights of the polyolefins employed in the present invention, which are defined by precise viscosity average molecular weights.

In particular, the present invention relates to the use of particles comprising an ultra-
15 high-molecular-weight polyolefin as proppants for treating a subterranean formation, wherein the ultra-high-molecular-weight polyolefin has a viscosity average molecular weight ranging from 0.8×10^6 to 12×10^6 g/mol, an apparent density lying in the range from 0.2 to 0.7 g/mL, and wherein the sphericity of the particles is 0.5 or higher.

As used herein, the term “polyolefin” also includes blends of different polyolefins and
20 blends of polyolefins with any other polymeric material. Preferably, the proportion of ultra-high molecular weight polyolefin in the blend is at least 90% wt, even more preferably is of at least 95% wt. In a more preferred embodiment, the ultra-high molecular weight polyolefin is a homopolymer of a particular ultra-high molecular weight polyolefin.

25 As used herein, the term “polyolefin” also includes functionalized polyolefin, i.e. a polyolefin having additional chemical functionality, obtained through either copolymerization of olefin monomer with a functional monomer, or through graft copolymerization subsequent to olefin polymerisation. Typically, such functionalized groups include but are not limited to O, N, S, P, or halogen heteroatoms. Such reactive
30 functionalized groups include but are not limited to carboxylic acid, hydroxyl, amide, nitrile, carboxylic acid anhydride, or halogen groups.

The properties of the ultra-high molecular weight polyolefin make the particles used in the invention particularly advantageous as proppants. Thus, the particles used in the present invention are also referred to as proppant particles.

In any of the embodiments of the present invention, the ultra-high molecular weight polyolefin is preferably ultra-high molecular weight polyethylene or ultra-high molecular weight polypropylene. In a particular embodiment, the ultra-high molecular weight polyolefin is ultra-high molecular weight polyethylene. In another particular embodiment, the ultra-high molecular weight polyolefin is ultra-high molecular weight polypropylene.

The particles used in the present invention comprise ultra-high molecular weight polyolefin macromolecules which are inherently considerably viscous. Particularly, the viscosity average molecular weight of the ultra-high molecular weight polyolefin ranges from 0.8×10^6 to 12×10^6 . Viscosity average molecular weights can be calculated by methods known in the art. For instance, viscosity average molecular weights may be calculated from the intrinsic viscosity $[\eta]$ of the ultra-high molecular weight polyolefin as measured according to known standards. In the context of the present invention intrinsic viscosity is measured according to ASTM D4020-11. For instance, in the context of the present invention, the Margolies-equation is applied to determine ultra-high molecular weight polyethylene molecular weights according to ASTM D4020-11:

$$M_w = 5.37 \times 10^4 \times [\eta]^{1.49}$$

where M_w = viscosity average molecular weight (g/mol); $[\eta]$ = intrinsic viscosity (dl/g), measured according to ASTM D4020-11.

In an embodiment, the viscosimetric average molecular weight of the ultra-high molecular weight polyolefin ranges from 0.8×10^6 to 10×10^6 g/mol as calculated by the same method. In another embodiment, it ranges from 0.8×10^6 to 8×10^6 g/mol. In another embodiment, it ranges from 0.8×10^6 to 6.7×10^6 g/mol. In another embodiment, it ranges from 2×10^6 to 12×10^6 g/mol. In another embodiment, it ranges from 2×10^6 to 10×10^6 g/mol. In another embodiment, it ranges from 2×10^6 to 8×10^6 g/mol. In another embodiment, it ranges from 2×10^6 to 6.7×10^6 g/mol. In another embodiment, it ranges from 2.09×10^6 to 12×10^6 g/mol. In another embodiment, it ranges from 2.09×10^6 to 10×10^6 g/mol. In another embodiment, it ranges from 2.09×10^6 to 8×10^6 g/mol. In

- 6 -

another embodiment, it ranges from 2.09×10^6 to 6.7×10^6 g/mol. In another embodiment, it ranges from 2.18×10^6 to 12×10^6 g/mol. In another embodiment, it ranges from 2.18×10^6 to 10×10^6 g/mol. In another embodiment, it ranges from 2.18×10^6 to 8×10^6 g/mol. In another embodiment, it ranges from 2.18×10^6 to 6.7×10^6 g/mol.

5 By virtue of the ultra-high molecular weights of the polyolefins used in the particles of the invention, the use of additives to improve fracture fluid viscosity is diminished in the context of the present invention. Therefore, in a particular embodiment, the composition of the invention as described below does not comprise or comprises reduced amounts of viscosity enhancing agents.

10 Additionally, the particles used in the invention are strong in the sense that they are hard to fragment under high levels of stress, leading to a low generation of fines, ultimately maintaining the fracture highly conductive over time. Moreover, the reduction in fine generation provides for a lesser extent of impurities leaked into the extracted fluid.

The particles used in the invention are relatively low-density particles. Particularly, the
15 ultra-high molecular weight polyolefin comprised in the particles of the invention has an apparent density lying in the range from 0.2 to 0.7 g/mL. In another embodiment, the apparent density lies in the range from 0.2 to 0.6 g/mL. In another embodiment, the apparent density lies in the range from 0.2 to 0.54 g/mL. In another embodiment, the apparent density lies in the range from 0.2 to 0.5 g/mL. In another embodiment, it lies in
20 the range from 0.3 to 0.7 g/mL. In another embodiment, it lies in the range from 0.3 to 0.6 g/mL. In another embodiment, it lies in the range from 0.3 to 0.54 g/mL. In another embodiment, it lies in the range from 0.3 to 0.5 g/mL. In any of these embodiments, or in a particular embodiment, the ultra-high molecular weight polyolefin comprised the particles of the invention has an absolute density of less than 1.0 g/mL.

25 In the context of the present invention, apparent density is determined according to ISO 60:1977. In the context of the present invention, absolute density is determined according to ISO 1183-1:2012.

The hydrophobic nature and described densities of the ultra-high molecular weight polyolefin confers to the particles a series of advantages over classical proppants or
30 other polyolefins, including non-ultra-high molecular weight polyolefins, among which advantages the following stand out:

- 7 -

- High pumping or injecting rates are not required in order to impart a sufficient velocity to place the proppant further far from the wellbore into the fracture. This implies a reduction in energy consumption needed to pump the proppant laden slurry and a lessening of acoustic contamination.
- 5 - When using ultra-high molecular weight polyolefin proppant, a lower mass of proppant is required to achieve any desired fracture geometry when compared to the mass required with conventional proppants, implying reduced transportation costs and lower slurry volumes with consequent savings in energy and reduced environmental impact.
- 10 - The proppant particles do not tend to sink to the bottom of the fracture but rather float in most water based treatment fluids, thus achieving a more uniform distribution of the proppant throughout the fracture, which improves conductivity of the propped fracture when compared with conventional proppants whose density exceeds that of water.

- 15 The shape of the particles used in the invention is typically substantially spherical, which further improves particle-particle interstitial permeability and hence the conductivity of the fracture.

In the present invention, the sphericity of any of the particles described herein is at least 0.5. In a particular embodiment, the sphericity of the particles is at least 0.7. Since it is
20 exceedingly difficult to obtain perfectly spherical particles, i.e. with a sphericity value of 1, in a preferred embodiment, the particles are substantially spherical particles. Particles with minor deviations from a perfectly spherical shape are considered to be substantially spherical.

In the context of the present invention, sphericity is determined according to ISO
25 13503-2:2006

Additionally, in another embodiment of the invention, the particles display a roundness of 0.5 or higher, which further improves their permeability and hence the conductivity of the fracture. In a particular embodiment, the particles display a roundness ranging from 0.7 to 1.

30 In the context of the present invention, roundness is determined according to ISO 13503-2:2006.

- 8 -

In a particular embodiment, the particles display a sphericity and roundness as described immediately above.

The size of the particles of the present invention may depend, for example, on the characteristics of the subterranean formation selected for a fracturing and propping operation and completion design (size of perforations) to avoid in any of the cases near wellbore proppant bridge formation.

In addition, the particles of the invention display a narrow size distribution, which ensures that fracture stress is uniformly resisted by the particles throughout the whole fracture, thus contributing to enhanced fracture conductivity. The span value is an indicator for the width of particle size distribution and is based on the 10%, 50% and 90% particle size quantiles as follows:

$$\text{Span} = (D(0.9) - D(0.1)) / D(0.5)$$

where $D(0.5)$ is the volume median diameter value of the particle size in a given particle population, where the volume median diameter of 50% of the particles in the population is below this value and 50% is above the value; $D(0.1)$ is the value of the particle size in a given particle population, where the volume median diameter of 10% of the particles in the population is below this value and 90% is above the value; and $D(0.9)$ is the value of the particle size in a given particle population, where the volume median diameter of 90% of the particles in the population is below this value and 10% is above the value.

A perfect monodisperse distribution would have a span of zero. The particles of the present invention suitably have a near monodisperse size distribution in that the particles display a particle size distribution span value not higher than 1.8. In a particular embodiment, the span value ranges between 0.6 and 1.8. In another particular embodiment, the span value ranges between 0.85 and 1.8. In another particular embodiment, the span value ranges between 0.97 and 1.8.

In a particular embodiment, the particle size distribution is unimodal. In another embodiment, it is bimodal. In another embodiment it is polymodal, e.g. trimodal.

In the context of the present invention, size distribution is determined according to ISO 13320:2009.

- 9 -

Advantageously, the density and size distribution of the particles used in the invention allow the placement of a partial monolayer of proppant particles along the fracture, as defined by S. R. Darin and J. L. Huitt, SPE-1291G, 1960.

In an embodiment of the present invention, the combination of the above described viscosity average molecular weights of the polyolefin comprised in the particles of the invention, along with the above described particle size distribution span values provides a proppant pack permeability of higher than $2.9607699 \times 10^{-15} \text{ m}^2$ (0.003 Darcys), as measured according to ISO 13503-5:2006 at a closure pressure of 13789514.56 Pa (2000 psi) (1 psi = 6894.75729 Pa). In another embodiment, the permeability is 4.44115485 $\times 10^{-15} \text{ m}^2$ (0.0045 Darcys) or higher. In another embodiment, the permeability ranges between higher than $2.9607699 \times 10^{-15} \text{ m}^2$ (0.0030 Darcys) and $2.9607699 \times 10^{-11} \text{ m}^2$ (30 Darcys). In another embodiment, it ranges between $4.44115485 \times 10^{-15} \text{ m}^2$ (0.0045 Darcys) and $2.9607699 \times 10^{-11} \text{ m}^2$ (30 Darcys). In another embodiment, the permeability ranges between higher than $2.9607699 \times 10^{-15} \text{ m}^2$ (0.0030 Darcys) and $1.9738466 \times 10^{-14} \text{ m}^2$ (0.0200 Darcys). In another embodiment, it ranges between $4.44115485 \times 10^{-15} \text{ m}^2$ (0.0045 Darcys) and $1.77646194 \times 10^{-14} \text{ m}^2$ (0.0180 Darcys). Advantageously, for a given proppant pack width the good permeabilities of the particles of the present invention allow achieving enhanced proppant pack conductivities, ultimately increasing productivity of fluid extraction. Proppant pack conductivity can be expressed as follows: kWf , where

k is the proppant pack permeability, expressed in millidarcys;

Wf is proppant pack width, expressed in feet.

As known by the skilled person, 1 Darcy is equivalent to $9.869233 \times 10^{-13} \text{ m}^2$; and 1 foot is equivalent to 0.3048 m.

In the present text, values presented in SI units, followed in brackets by the corresponding value and unit in which the measurements are usually expressed/measured in the field of the invention. In case of any inconsistency, values and units in brackets should prevail. As mentioned above, conversion amongst units is general common knowledge.

In another particular embodiment, the particles used in the invention are porous, such that extracted fluid can flow through the proppant particles rather than just through the

- 10 -

interstitial spaces. In an embodiment of the invention, the particles of the invention display a porosity between 2 and 50% by volume as determined by measurement of the ratio of the effective density of individual particles divided by the density of the solid material. This means that from 2 to 50% of the volume of the particles is in the form of pores. In the context of the present invention, porosity is measured according to ASTM D4222-03(2008) or ASTM D4284-12.

The particles used in the present invention display a slight deformability sufficient to prevent shattering of the particles under the closure pressure applied by a fracture. Moreover, the slight deformability of the particles of the invention is such that it reduces the chances of proppant backflow taking place.

By virtue of their mechanical properties, the particles of the invention typically display a crush resistance of between 0 and 5% at 27579029.12 Pa (4000 psi) as measured according to ISO 13503-2:2006.

In a particular embodiment of the invention, the particles comprise no additives.

In another particular embodiment, the particles used in the present invention can be treated with a coating and/or penetrating material using any suitable wet or dry process, such that the properties of the particles are selectively modified.

Thus, in a particular embodiment, the particles used in the present invention further comprise a coating material. Preferably, this coating material has a Tg of at least 80°C, more preferably between 80 and 120°C in order to provide, for example, particle strength and to reduce *in situ* fine migration. This coating material can be placed on the surface of the particles in the form of a monolayer or multilayer. The thickness of the coating layer is generally between 1 and 5 microns.

Non-limiting examples of coating materials that may be used to coat the particles described herein include resins and/or plastics. Specific examples of plastic include, but are not limited to, nylon, polystyrene, polyol esters, divinyl benzene polystyrene, etc. and combinations thereof. Suitable resins include phenol formaldehyde resins, melamine formaldehyde resins, urethane resins, epoxy resins, and mixtures thereof. In a particular embodiment, the particles of the invention are coated with an electrically conductive material. Non-limiting examples of electrically conductive materials that may be used for coating are metals, e.g. aluminum, copper or nickel; conductive

- 11 -

polymers, e.g. poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), polyanilines (PANI), and polypyrroles (PPY); and conductive nanoparticles, e.g. graphite, single or double-walled carbon nanotubes.

Methods for coating particles, such as fracture proppant particles, are known in the art and include spraying, sputtering, vacuum deposition, dip coating, extrusion, calendaring, powder coating, transfer coating, air knife coating, roller coating and brush coating.

In a particular embodiment, the coating material further comprises at least one filler. The coating material may comprises from 5% to 70%, preferably from 10 to 40% filler material by weight of the overall coating material. The relative amounts of filler may be adjusted by one skilled in the art to tailor the final proppant particles to achieve desirable physical properties, including particle density, bulk density, crush strength, etc.

The filler may have various morphologies, for example, isotropic, including spherical shapes, platy or acicular. The fillers may therefore be in the form of fibers, hollow or solid pellets or powders. In a particular embodiment, the filler may be any micro-sized particle that is compatible with the coating material and with the ultimate use of the particles as defined herein. In another embodiment, the filler may be any nano-sized particle that is compatible with the coating material and with the ultimate use of the particles as defined herein. In the context of the present invention “micro-sized particle” refers to particles with a size ranging from 1×10^{-7} to 1×10^{-4} m, whereas “nano-sized particle” refers to particles with a size ranging from 1×10^{-9} to 1×10^{-7} m.

In a particular embodiment, the filler comprises at least one of glass microbubbles, glass microspheres, silica, calcium carbonate, ceramic microspheres, aluminum silicate, carbon black, mica, micaceous iron oxide, aluminum oxide, radionuclides or feldspar. In a particular embodiment, the filler comprises zero-valent iron (Fe^0). In another particular embodiment, the filler comprises iron oxide.

In another particular embodiment, the particles used in the invention further comprise a penetrating material. By “penetrating material” should be understood a material that penetrates into the porous matrix of the particles impregnating their pores. The porosity and permeability characteristics of the particles used in the invention allows the

- 12 -

penetrating material to be drawn at least partially into the porous matrix of the particle by capillary action or by vacuum and/or pressure impregnation. For example, the particles may be immersed in a penetrating material and then exposed to pressure and/or vacuum to at least partially penetrate or impregnate the material.

- 5 The penetrating material may be selected so that it helps to structurally support the matrix of the porous particles, i.e., increases the strength of the particles, and increases the ability of particles to withstand the closure stresses of a hydraulic fractured formation or other downhole stresses.

For example, a penetrating material may be selected by balancing the need for low
10 apparent density versus the desire for strength, since a more dense material may provide much greater strength. In this regard, the inherent porosity of the particles used in the invention may be altered so as to help provide the desired balance between apparent density and strength. It should be noted however that the inherent properties of the particles of the invention are such that no density-increasing agents are generally
15 needed.

Non-limiting examples of penetrating materials that may be used with the particles used in the present invention include, but are not limited to, resins, plastics, cements, sealants, binders or any other material or combination of any of these materials suitable for at least partially penetrating the porous matrix of the particles used in the invention
20 to provide, for example, improved characteristics of strength/crush resistance. Specific examples of plastic include, but are not limited to, nylon, polystyrene, polyol esters, divinyl benzene polystyrene, etc. and combinations thereof. Suitable resins include phenol formaldehyde resins, melamine formaldehyde resins, urethane resins, epoxy resins, and mixtures thereof.

- 25 The extent of penetration of the penetrating material in the particles is from less than about 1% penetration by volume to more than 25% penetration by volume.

In a particular embodiment, the particles used in the present invention comprise at least one coating material and at least one penetrating material, in any combination from the foregoing lists.

- 30 In a particular embodiment, the coating material as described above can also be used as penetrating material as it also penetrates within the porous matrix of the particles.

- 13 -

The coating material and/or penetrating material is generally present in the particles in an amount from about 0.5% to about 10% by weight on the basis of the total weight of the particle.

Ultra-high molecular weight polyolefins according to the present invention may be prepared employing different methods known in the art, non-limiting examples of which are mentioned below. Shamiri *et al.* (Materials, 2014, 7, 5069-5108) review the influence of Ziegler-Natta and metallocene catalysts on polyolefin structure, including their influence on the control of the molecular weight of said polyolefins. EP0626393 describes a process for the preparation of spherical polyolefins, and particularly ultra-high molecular weight polyethylene, under a specific Ziegler-Natta catalyst system. EP0878490 further reports a loop/slurry process for the preparation of ultra-high molecular weight olefin polymers in the absence of hydrogen. EP0683178 describes a process for the preparation of ultra-high molecular weight polyethylene in homopolymeric form or as copolymers with other olefins, and with narrow particle size distributions. JPH07292021 describes a process for the preparation of ultra-high molecular weight polypropylene. Particularly preferred in the context of the present invention is the preparation of ultra-high molecular weight polyolefins according to the well-known Mitsui CX process, a slurry phase polymerization which takes place in a two-reactor system (reviewed in JM Asua, Polymer Reaction Engineering, 2007, 105-106). The teachings of all the above documents are herein incorporated by reference.

Ultra-high molecular weight polyolefins are also commercially available. For example suppliers of ultra-high molecular weight polyethylene include Ticona (e.g. GUR 2122, 4113, 4120, 4130, 4150, 4152, 4170, GUR GHR 8020, 8110), Koninklijke DSM N.V./Royal DSM (e.g. Stamylan UH034, UH210, UH410, UH610), Braskem (e.g. UTEC 3040, 3041, 6540, 6541, IDEALIS 500), Mitsui Chemicals (e.g. HI-ZEX MILLION 030S, 145M, 240S, 240M, 320MU, 340M, 341L, 630M, MIPELON XM220, XM221U, PM200), Reliance Industries Ltd. (e.g. Relene Ultra 2504).

The particles used in the present invention may be used alone or as part of a composition. Therefore, the present invention also refers to a composition comprising the particles as described herein, and a fracturing fluid. Methods for combining proppant particles and fracturing fluids into fracturing compositions are well-known to

- 14 -

the person skilled in the art. For example the components of the fracturing composition may be combined in a vessel such as a mixer, blender, and the like such as to achieve mixing, agitation or stirring of the components. In some embodiments, the components of the fracturing composition are injected into the fracture “on the fly”, i.e. the components are combined as they are being injected into the fracture.

In the present invention the term “fracturing fluid” or “treatment fluid” has the meaning generally understood by the person skilled in the art, and refers to any fluid capable of carrying the particles described herein into fractures. In an embodiment, the fracturing fluid is selected from water based fluids such as fresh water, sea water, sodium chloride brines, calcium chloride brines, potassium chloride brines, sodium bromide brines, calcium bromide brines, potassium bromide brines, zinc bromide brines, ammonium chloride brines, tetramethyl ammonium chloride brines, sodium formate brines, potassium formate brines, cesium formate brines; water based polymer and polymer containing fluids such as hydroxypropyl guar (HPG), carboxymethylhydroxypropyl guar (CMHPG), carboxymethyl guar (CMG), hydroxyethyl cellulose (HEC), carboxymethylhydroxyethyl cellulose (CMHEC), carboxymethyl cellulose (CMC), starch based polymers, xanthan based polymers, and biopolymers such as gum arabic, carrageenan, and the like; non-aqueous fluids such as methanol, ethanol, isopropanol, and other branched and linear alkyl alcohols, diesel, raw crude oils, condensates of raw crude oils, refined hydrocarbons such as gasoline, naphthalenes, xylenes, toluene and toluene derivatives, hexanes, pentanes, and ligroin, natural gas liquids; gases such as carbon dioxide, nitrogen, propane, methane, butane; or combinations or derivatives of any of the foregoing fluids.

In a particular embodiment, the fracturing fluid is selected from a water based fluid, a linear or branched alcohol or mixtures thereof, and gases, particularly methane, propane, nitrogen or carbon dioxide.

The particles of the invention are hydrophobic in nature, which is particularly advantageous when polar fracturing fluids are employed. Repulsion forces between the particles and the fluid induce the formation of an air film around the particles, thus enhancing their transportability into the subterranean fractures and increasing the hydrostatic forces which cause a tendency for the proppant particles to float in the

- 15 -

treatment fluid due to their low density.

Therefore, in a particular embodiment, the fracturing fluid is a polar fracturing fluid. In a particular embodiment, the polar fracturing fluid is selected from water based fluids, even more preferably the fracturing fluid is fresh or brackish water, optionally
5 comprising a minimal concentration of other chemicals dissolved or mixed into the water.

The good inherent properties of the particles disclosed herein allow successfully employing the particles as defined in any of the different embodiments described above in a composition without the need to include additives to improve the density or
10 viscosity of the fracturing composition of the invention. Therefore, in a particular embodiment of the invention, the composition of the invention does not include any viscosity-modifying agent, preferably it does not include any viscosity-increasing agent. Non-limiting examples of viscosity-modifying agents are guar gum, hydroxypropylguar, hydroxyethylcellulose, xanthan,
15 carboxymethylhydroxypropylguar, diutan, chitosan, or cationic, anionic, nonionic, mixed, zwitterionic or amphoteric surfactants. In another particular embodiment, the composition of the invention does not include any density-modifying agent, preferably it does not include any density-increasing agent. Non-limiting examples of density-modifying agents are silicates, phosphates, borates, fly ash, glass, glass microspheres,
20 ceramic microspheres, aluminosilicates, silica (quartz sand), alumina, mica, kaolin, hematite, calcium carbonate, calcium chloride, calcium bromide, barium sulfate, an alkali metal salt, talc, zirconia and trimanganese tetraoxide. In a particular embodiment, it neither comprises any viscosity-modifying agent nor any density-modifying agent. In a more particular embodiment, the composition of the invention consists of the particles
25 as defined in any of the above mentioned embodiments, and a fracturing fluid. Under these embodiment, less chemical substances are employed as compared with other proppant laden fluids, thus reducing any potential for waste contamination as well as material costs.

However, it should be noted that the present invention also refers to compositions
30 comprising the particles as defined in any of the different embodiments described above and a fracturing fluid, the composition further comprising one or more proppants and/or

- 16 -

additives.

Therefore, in a different embodiment, the composition of the invention comprises one or more additional proppant particles, not limited to those described in the present invention. The term proppant particles as employed herein is that generally understood
5 by the person skilled in the art.

The additional proppant particles referred to above may include in specific embodiments one or more of the following materials; sand, sand, glass, ceramic, metallic or polymer-based materials, graded nut shells, resin-coated nut shells, sintered bauxite, particulate ceramic materials, glass beads, and particulate thermoplastic or
10 thermoset polymers.

Mixing other proppants and the proppant particles described herein may be useful, for example, for reducing the cost of proppants while maintaining at least some of the beneficial properties of the particles described herein.

In a different embodiment, the composition of the invention comprises one or more
15 additives which serve the purpose of adapting the properties of the composition to particular kinds of subterranean formations. In a particular embodiment, the additive or additives are selected from the group consisting of a fluid loss control additive, a lost circulation material, a surfactant, a salt, a formation conditioning agent, a foaming agent, an acid, non-emulsifier, solvents, breakers, a biocide, an algicide, crosslinking
20 agent, gelling agent, pH buffer, viscoelastic surfactant, friction reducer, a flow enhancing additive, and combinations thereof.

As mentioned previously, the present invention is also directed to a method for treating a subterranean geological formation penetrated by a wellbore, the method comprising pumping or injecting into the wellbore a plurality of particles as defined herein or a
25 composition according to any of the above embodiments.

In a particular embodiment, the method for treating a subterranean geological formation is a method of fracturing a subterranean geological formation.

The plurality of particles or the composition is injected at a pressure sufficient to create a new fracture or to open an existing fracture in the formation. At least a portion of the
30 particles is placed in the fracture, maintaining the integrity thereof. As described above,

- 17 -

the properties of the particles used in the invention are such that relatively low pumping or injecting rates may be used in the method of the invention.

In a particular embodiment, the method for treating a subterranean geological formation penetrated by a wellbore comprises pumping or injecting into the wellbore a
5 composition according to any of the above embodiments.

Thus, in one embodiment the invention provides a method of treating a subterranean geological formation comprising the steps of providing a composition comprising the particles as defined herein and a fracturing fluid, placing the composition into the subterranean formation at a pressure sufficient to create or enhance at least one fracture
10 therein.

Still another embodiment provides a method of hydraulic fracturing a subterranean geological formation comprising the steps of providing a composition comprising the particles as defined herein and a fracturing fluid, placing the composition into the subterranean formation at a pressure sufficient to create or enhance at least one fracture
15 therein.

EXAMPLES

The invention is illustrated by way of the following examples which are not intended to restrict its scope.

The following examples illustrate the behaviour of organic proppant particles
20 comprising at least one ultra-high molecular weight polyolefin with controlled properties depending on the selected polymer composition.

Particle Characterization

The following properties and corresponding standards were employed in the characterization of the particles according to the present invention. Particularly,
25 apparent density was measured according to ISO 60:1977; the melting temperature and crystallinity by Differential Scanning Calorimetry (DSC) according to UNE-EN ISO 11357-1:2010 and ISO 11357-3:11; absolute density according to ISO 1183-1:2012; Intrinsic Viscosity, standardized by ASTM D4020-11 and molecular weight according to Margolies' equation; sphericity, roundness and crush resistance according to ISO
30 13503-2:2006/API RP19C:2008; long-term conductivity and permeability according to

- 18 -

ISO 13503-5:2006/ API RP 19D.

Other parameters were determined according to internal methods or using conventional techniques. Particularly, average particle size and particle size distribution were determined by using a particle size analyzer (Mastersizer) available from Malvern

5 Instrument Ltd a Spectris Company.

Thus, the particle size analyses were recorded on a Mastersizer analyzer that use laser diffraction technique. The samples were dispersed in air (dry form) and the intensity of the light scattered at different angles were collected when a laser beam passes through.

Thus, three kinds of data were determined: the particle size, the particle size distribution
10 and the uniformity, which were assigned according to ISO-13320, ASTM-D-1921 or ASTM-D-4464. In particular, D(0.9), D(0.1), D(0.5) and D(4.3) were calculated, where D(0.9), D(0.1), D(0.5) are as described above and D(4.3) is the volume or mass moment mean or the De Broucker mean, in particular the volume mean. The D(4.3) value is the arithmetic average of the particle population.

15 *Commercial Ultra High Molecular Weight Polyolefins*

Examples C1-C5: Commercial Ultra High Molecular Weight Polyolefins according to the invention

Examples consisted of the following ultra-high molecular weight polyolefins: UTEC 3040 (supplied commercially by Braskem as a powder), GUR 2122, GUR 4113, GUR
20 4170 and GUR 4120 (supplied commercially by Ticona (now Celanese)). The physical properties of these polyolefins are summarized in Table 1. In particular, differential Scanning Calorimetry (DSC) shows a low crystallinity as expected for ultra-high molecular weight polymers.

Example CE1: Commercial High Molecular Weight Polyolefin (comparative example)

25 Comparative example consisted of GHR 8110 supplied commercially by Ticona as a High Molecular Weight PE grade. The physical properties of the commercial High Molecular Weight PE are summarized in Table 1. In particular, Differential Scanning Calorimetry (DSC) shows a medium crystallinity as expected for high molecular weight polymers.

Table 1: Properties of Commercial Ultra High Molecular Weight Polymers and Comparative Example of
Commercial High Molecular Weight Polymer

Name	Example	T _m , °C	Cristallinity %	Apparent Density (g/ml)	Mw (10 ⁶ g/mol)	D(0,1)	D(0,5)	D(0,9)	D(4,3)	Span
UTEC 3040	C1	133	50.5	0.52	2.58	104.93	175.68	277.83	184.43	0.98
GUR2122	C2	133	50.8	0.30	2.18	53.64	146.49	321.87	170.78	1.80
GUR4113	C3	133	54.0	0.51	2.74	77.50	128.25	202.85	134.94	0.97
GUR4170	C4	133	48.3	0.54	6.70	76.54	131.02	208.52	137.15	1.00
GUR4120	C5	132	51.2	0.53	2.09	75.90	119.08	177.85	123.39	0.85
GHR8110	CE1	132	62.3	0.52	0.64	68.21	113.92	178.94	119.14	0.97

- Compared to the high molecular weight polyolefin, ultra-high molecular weight polyolefin particles according to the present invention provide higher conductivity and crush resistance, ultimately allowing improved gas or liquid propagation. In addition, these polyolefin particles have excellent apparent and absolute density. Therefore, a good balanced permeability and sustainability was obtained in the ultra-high molecular weight polyolefin particles of this invention.
- 10 In particular, the polyolefin particles of Examples C1-C4 and CE1 were used for single-point Long-term Conductivity test comparisons (Table 2). Thus, resins according to this invention have good crush resistance and conductivity measured according to ISO 13503-2:2006/API RP19C:2008 and ISO 13503-5:2006/API RP 19D. Therefore, these Ultra High Molecular Weight polyolefin particles are in agreement with proppant requirements and are suited for hydraulic fracturing, in particular conventional or non-conventional fracturing techniques.

- 20 -

Table 2: Long-Term Conductivity, permeability and width at 13789514.56 Pa (2000 psi) and 65.55 °C (150 °F) for examples according to the invention C1-C4 and comparative CE1.

API Long-Term Conductivity Test					
Permeability at 65.55 °C (150 °F), m²					
Closure Pressure, Pa	UTEC 3040 C1	GUR4113 C3	GUR4170 C4	GUR2122 C2	GHR8110 CE1
13789514.56 (2000 psi)	1.77646194x10 ⁻¹⁴ (0.0180 Darcy)	1.08561563 x10 ⁻¹⁴ (0.0110 Darcy)	7.20454009 x10 ⁻¹⁵ (0.0073 Darcy)	4.44115485x10 ⁻¹⁵ (0.0045 Darcy)	2.9607699x10 ⁻¹⁵ (0.0030 Darcy)
Pack Width at 65.55 °C (150 °F), mm					
13789514.56 (2000 psi)	6.19	6.03	6.30	6.11	5.89
Conductivity at 65.55 °C (150 °F), mm²*m					
13789514.56 (2000 psi)	1.082931199 x10 ⁻¹³ (0.360 mD*ft)	6.61791288 x10 ⁻¹⁴ (0.220 mD*ft)	4.512213328 x10 ⁻¹⁴ (0.150 mD*ft)	2.737409419 x10 ⁻¹⁴ (0.091 mD*ft)	1.744722487 x10 ⁻¹⁴ (0.058 mD*ft)

CLAIMS

1. Use of particles comprising an ultra-high-molecular-weight polypolyolefin as proppants for treating a subterranean formation, wherein the ultra-high-molecular-weight polyolefin has a viscosity average molecular weight ranging from 0.8×10^6 to 12×10^6 g/mol; an apparent density lying in the range from 0.2 to 0.7 g/mL; and wherein said particles have a sphericity of 0.5 or higher.
2. Use according to claim 1, wherein the ultra-high molecular weight polyolefin is ultra-high molecular weight polyethylene or ultra-high molecular weight polypropylene.
3. Use according to any of the preceding claims, wherein the viscosity average molecular weight of the ultra-high-molecular-weight polyolefin ranges from 2×10^6 to 10×10^6 g/mol.
4. Use according to any of the preceding claims, wherein the ultra-high-molecular-weight polyolefin has an apparent density lying in the range from 0.3 to 0.5 g/mL.
5. Use according to any of the preceding claims, wherein the particles have a sphericity of at least 0.7.
6. Use according to any of the preceding claims, wherein the particles have a porosity between 2 and 50% by volume.
7. Use according to any of the preceding claims, wherein the particles further comprise a coating material.
8. Use according to claim 7, wherein the coating material comprises an electrically conductive material.
9. Use according to claim 8, wherein the electrically conductive material is a metal.
10. Use according to any of the preceding claims, wherein the particles further comprise a penetrating material.
11. Use according to claims 7 to 10, wherein the coating and/or penetrating material comprises a plastic and/or a polymeric resin, and wherein the plastic is selected from nylon, polystyrene, polyol esters, divinyl benzene polystyrene and combinations thereof, and wherein the polymeric resin is selected from phenol formaldehyde resins, melamine formaldehyde resins, urethane resins, epoxy resins, and mixtures thereof.
12. A composition comprising particles as defined in any of the preceding claims and a

- 22 -

fracturing fluid suitable for carrying the particles.

13. Composition according to claim 12, wherein the fracturing fluid is water, a linear or branched alcohol or mixtures thereof, or a gas selected from a hydrocarbon based-gas, carbon dioxide and nitrogen.
- 5 14. Composition according to claim 12 or 13, further comprising one or more additional proppant particles.
15. Method for treating a subterranean geological formation penetrated by a wellbore, the method comprising pumping or injecting into the wellbore a plurality of particles as defined in any of claims 1-11 or a composition as defined in any of
10 claims 12-14.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/054004

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/88 E21B43/267
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 E21B

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.
A	US 2013/092374 A1 (FULTON ROBERT GORDON [CA] ET AL) 18 April 2013 (2013-04-18) cited in the application the whole document	1-15
A	US 2008/060809 A1 (PARKER MARK A [US] ET AL) 13 March 2008 (2008-03-13) cited in the application the whole document	1-15
A	WO 2010/021563 A1 (WILLBERG DEAN [US]; FREDD CHRIS N [US]; GOLOSHCHAPOVA DINA ANDREEVNA []) 25 February 2010 (2010-02-25) the whole document	1-15
A	US 2006/151170 A1 (BRANNON HAROLD D [US] ET AL) 13 July 2006 (2006-07-13) the whole document	1-15
	-/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"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

15 April 2016

Date of mailing of the international search report

02/05/2016

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

Nemes, Csaba A.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/054004

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013/036350 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; HONG LIANG [US]; JOHNSON AARON M [US] 14 March 2013 (2013-03-14) cited in the application the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/054004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013092374 A1	18-04-2013	AU 2006200745 A1	06-09-2007
		CA 2536957 A1	03-03-2007
		US 2007193745 A1	23-08-2007
		US 2009107672 A1	30-04-2009
		US 2011088900 A1	21-04-2011
		US 2012090840 A1	19-04-2012
		US 2013092374 A1	18-04-2013
US 2008060809 A1	13-03-2008	US 2006048943 A1	09-03-2006
		US 2008060809 A1	13-03-2008
WO 2010021563 A1	25-02-2010	AU 2008360718 A1	25-02-2010
		CA 2735572 A1	25-02-2010
		CN 102159791 A	17-08-2011
		EP 2324196 A1	25-05-2011
		RU 2011110576 A	27-09-2012
		US 2011180259 A1	28-07-2011
		US 2015204178 A1	23-07-2015
		WO 2010021563 A1	25-02-2010
US 2006151170 A1	13-07-2006	CA 2497948 A1	12-07-2006
		CA 2715597 A1	12-07-2006
		US 2006151170 A1	13-07-2006
		US 2008110623 A1	15-05-2008
		US 2011000667 A1	06-01-2011
WO 2013036350 A1	14-03-2013	CA 2845011 A1	14-03-2013
		CO 6880060 A2	28-02-2014
		EP 2742110 A1	18-06-2014
		RU 2014109367 A	20-09-2015
		US 2014202696 A1	24-07-2014
		WO 2013036350 A1	14-03-2013