Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2717640 C 2015/02/10

(11)(21) 2 717 640

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 2010/10/15
(41) Mise à la disp. pub./Open to Public Insp.: 2011/04/15
(45) Date de délivrance/Issue Date: 2015/02/10
(30) Priorité/Priority: 2009/10/15 (CA2,682,902)

(51) Cl.Int./Int.Cl. *C09K 8/80* (2006.01), *E21B 43/267* (2006.01)

(72) Inventeurs/Inventors:
PEYCHEV, VIKTOR GEORGIEVICH, RU;
PLINER, SERGEY YOURIEVICH, RU;
SHMOTIEV, SERGEY FEDOROVICH, RU;
SYCHEV, VYACHESLAV MIKHAILOVICH, RU;
ROZHKOV, EVGENY VASSILIEVICH, RU

(73) Propriétaire/Owner:
ILEM RESEARCH AND DEVELOPMENT EST., LI

(74) Agent: BCF LLP

(54) Titre : METHODE DE FABRICATION D'AGENTS DE SOUTENEMENT EN SILICE
(54) Title: SILICEOUS PROPPANT PROCESS OF MANUFACTURE

(57) Abrégé/Abstract:
A process for the production of siliceous ceramic proppants having a high percentage of SiO_2 (preferably 71 mass.% and more) and meant for oil industry as propping agents used during hydraulic fracturing process.

SILICEOUS PROPPANT PROCESS OF MANUFACTURE

ABSTRACT OF THE DISCLOSURE

A process for the production of siliceous ceramic proppants having a high percentage of SiO_2 (preferably 71 mass.% and more) and meant for oil industry as propping agents used during hydraulic fracturing process.

TITLE OF THE INVENTION

SILICEOUS PROPPANT PROCESS OF MANUFACTURE

FIELD OF THE INVENTION

The subject of the invention refers to the production of siliceous ceramic proppants having a high percentage of SiO_2 (preferably 71 mass.% and more) and meant for oil industry as propping agents used during hydraulic fracturing process.

BACKGROUND OF THE INVENTION

Proppants are solid spherical granules preventing cracks in oil wells from closing due to over high pressure and ensuring the necessary productivity of oil wells by creating a conductive channel in the layer.

Different organic and non-organic materials are used as proppants: walnut shells, sand, resin-coated sand, etc. However, due to the particularities of their microstructure ceramic proppants are of primary use because their main characteristics determined by ISO 13503-2:2006(E) requirements (granulometry, sphericity, roundness, crush resistance, density, acid solubility, turbidity of fracturing fluid wetting proppants) surpass other products used in hydraulic fracturing processes.

Among ceramic proppants, silica-alumina and silica-magnesia proppants are the most common. Siliceous proppants are less present on the market. The flow sheets of ceramic proppants production are similar in the majority of cases and include charge make-up (as a rule mixing of pre-grinded original components in specified ratio), its granulation and high-temperature burning to obtain the maximum density and optimize chemical and phase composition of ceramics.

Crush resistance and turbidity of fracturing fluid wetting proppants are very important processing factors determining their consumer properties. Turbidity index specifies the number of fine-dispersed particles suspended in the wetting fluid. The higher this index is, the higher the quantity of suspended particles in the fluid is.

Fine-dispersed dust forms during proppants sieving, packing, transportation and feeding into the well due to some attrition of their granules during contact.

A high content of dust-like particles results in their accumulation in the extraction channel of proppants pack and reduces its permeability.

In recent years researchers have aimed their efforts at searching for natural raw materials ensuring admissible values of the above-mentioned characteristics. In this context siliceous proppants rich in silicon dioxide and having a fair quantity of glass phase in the volume of granules and on their surface are particularly interesting.

A process is known for making ceramic proppants for oil wells manufacturing from magnesium silicate containing from 55 to 80% of forsterite. The material is gradually grinded, granulated and burned at 1150-1350^{0}C. (Russian Federation Patent No. 2 235 703).

The disadvantage of this known process is that proppants manufactured in this way have an increased index of turbidity of wetting fluid and insufficient factor of strength.

This is explained by the fact that the glass phase formed in these proppants is of low strength, non-uniformed by volume and has a coefficient of thermal linear expansion different from that of the master crystalline phase. Consequently, microfractures that are formed in volume and on proppant surfaces during its cooling reduce the solidity of the proppants and increase the turbidity of the wetting fluid.

United States Patent No. 6.753.299 sets out the advanced composition of lightweight proppants having less than 25% of alumina, 45% - 70% of silica and less than 10% of the binding agent wollastonite and talc (proportioning by weight).

This lightweight proppant is made by mixing grinded components of bauxite, quartz, shale and binding agents – talc and wollastonite. In addition starch and water are added to this mixture, which is subsequently granulated and burned. The burning is made at a temperature range of 1100– 1200^0 C.

A disadvantage of this known process is the increased index of turbidity of the wetting fluid and an insufficient strength. The reason is that wollastonite and talc used as binding agents form, together with other additives, fragile glass phase in proppant granules non-uniformed by volume and having a coefficient of thermal linear expansion different from that of the master crystalline phase.

SUMMARY OF THE INVENTION

Therefore, in accordance with the present invention, there is provided a process for the manufacture of siliceous proppants, comprising charge make-up by mixing reference grinded components, wherein a granulation and burning thereof differing in that at the stage of charge make-up, grinded inorganic fluoride is added in the quantity of 1-9 mass % and granule burning is made at a temperature range of between 950'C and 1050'C.

The above process is also novel in that the fractional content of grinded charge and inorganic fluoride is of 40 microns and less.

The above process is further novel in that the grinded inorganic fluoride is taken as a mono-compound and/or as a mixture of several fluorine-containing compounds.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS OF THE INVENTION

In general terms, the present invention addresses the technical problem by decreasing the wetting fluid turbidity during proppants use due to their strength increase by force of a general glass phase quantity growth and its more uniform distribution throughout the granule volume.

The mentioned result is obtained by adding grinded non-organic fluoride in the quantity of 1-9 mass.% at the stage of the charge mixture of the conventional process of siliceous proppants manufacture which includes its granulation and the burning of granules at the temperature range of 950 – 1050^{0}C.

The fractional composition of grinded charge and non-organic fluoride is 40 microns and less (during sieve analyses, not more than 1% being retained on a screen #004). In addition, grinded fluoride is taken as a mono-compound as well as a mixture of several non-organic fluorine-containing compounds.

It is known that the majority of raw materials used in the manufacture of siliceous proppants contain low-melting oxides (K_2O, Na_2O, etc.), which form a liquid phase while burning and arbitrarily distribute between grains of master crystalline phases in the form of amorphous glass phase of variable chemical composition when cooling.

Additionally, supplementary internal stress is formed in the volume of proppant granule due to the difference in the coefficient of thermal linear expansion between glass phase and crystalline phase. On application of external stress, fracture is developed in areas having the smallest resistance to fracture initiation and propagation. As amorphous glass phase has less strength properties in comparison to master crystalline phases, fracture of ceramic proppants is mainly of intergranular nature. Introduction of the abovementioned quantity of grinded non-organic fluoride in charge composition meant for siliceous proppants manufacture allows to reduce the turbidity of wetting fluid and to increase proppants strength by means of total glass phase quantity increase and its more equal volume distribution in proppant granule.

In the framework of the technical solution of the present invention, the following agents may be used as non-organic fluorides: fluorine-apatite, fluorite, potassium fluozirconate, sodium aluminum fluoride, etc.

Fluorine-containing non-organic compounds, being flux, reduce considerably the sintering temperature of proppants and may be used as sintering additives for ceramic mixtures meant for siliceous proppants production. In the process of glass and glassceramics manufacture, fluorides are used as an accelerator and as a catalyst of crystallization.

Thus, burning of siliceous proppants granules results in the quick formation of glass phase and the presence of F-ions in material led to the fact that amorphous glass phase crystallizes with considerably increased strength properties.

A further advantage is that the introduction of non-organic fluoride in specified quantities into ceramic charge for proppants manufacture does not require a supplementary crystallization as commonly used in glassceramics production practice. In addition, the presence of non-organic fluoride in material results in additional formation of increased quantity of glass phase in proppants volume and especially on their surface, which conduces in turn to the densification and abrasion resistance increase thereof.

The improvements in the operating characteristics of the proppants of the present invention, which are due to non-organic fluoride introduction into charge composition, is achieved only if the siliceous materials that are used have 71 mass % and more of SiO_2. This is due to the fact that the abovementioned charge has a large quantity of glass phase which is strengthened under the F-ions influence.

The choice of the type of fluoride is determined by the composition of its primary components and their balance.

The criteria of charge choice and burning temperature optimization are clear for specialists working in the industry of ceramic proppants production.

If the content of SiO_2 in the charge is less than 71 mass %, the total glass phase quantity in proppant volume is reduced thereby resulting in proppants density and strength decrease, and consequently in a turbidity rise of the wetting fluid.

Primary components and fluorine-containing additive grinding (40 microns and less) is made to obtain a more equal distribution of glass phase in proppant volume during burning.

Experience has shown that when using specified materials with particle sizes of more than 40 microns, there is formed a lot of melting marks on the proppant surfaces. In addition, proppants have increased turbidity of wetting fluid and decreased strength. This is likely to be related to the coefficient difference of thermal linear expansion between non-uniform large areas of glass phase and particles of crystal phase.

Introduction of fluorine-containing non-organic compounds in the charge in a quantity of less than 1 mass % does not have notable effect on proppants properties, and if their quantity is more than 9 mass % there results in the formation of a large number of cakes due to the abrupt increase of glass phase quantity.

Proppants burning at a temperature of less than 950^0C does not result in a sufficient densification of proppants granule when sintering. Consequently, the material has weak strength properties and increased turbidity of wetting fluid. At a burning temperature of more than 1050^0C, granules are alloyed.

A natural raw material that is particularly well suited for use in the realization of the technical solution of the present invention is feldspar quartz sand that has more than 71 mass % of SiO2. Russian sands from Pyshminskoe, Malyshevskoe and Nikolskoe deposits of the Sverdlovsk region were used to run experiments.

Examples of implementation of the present invention.

Example 1.

Proppants of silica-magnesia material (fraction 20/40 mesh) were manufactured in compliance with the present invention as follows: 1 kg of previously grinded material (fraction 40 microns and less) with forsterite content 55-80% (48-50 mass % of SiO_2) and 12 grams (1,2 mass %) of fluorine-apatite (fraction less than 40 microns) were placed in a dry-grinding mill. The components were mixed during 30 minutes, granulated and burned at different temperatures. Proppants trials with different percentages of fluorine-apatite were prepared similarly and burned at different temperatures sufficient for complete sintering of the proppants.

Example 2.

Proppants 20/40 mesh were manufactured in compliance with the present invention as follows: 1 kg of material having 21 mass % of Al_2O_3, 64 mass % of SiO_2, mixture of FeO, CaO, MgO, K_2O, TiO_2 material, (the rest is analogous to U patent № 6,753,299) were placed in dry-grinding mill; thereto were added 90 grams (9 mass %) of fluozirconate of sodium (fraction less than 40 microns). The components were mixed during 30 minutes, then granulated and burned at temperatures sufficient for complete proppants sintering.

Example 3.

20/40 mesh proppants of Pyshminsky deposit sand (86 mass.% - SiO_2, 8 mass.% - Al_2O_3, 3,2 mass.% - K_2O+N_2O, additives – the rest) and feldspar (67.5 mass.% - SiO_2, 17.3 mass.% - Al_2O_3, 12.2 mass.% - K_2O+N_2O, additives – the rest) were manufactured in compliance with the present invention as follows: 1 kg of previously grinded sand and feldspar (to have 40 microns fraction) in balance 9:1, 50 grams (5 mass%) of CaF_2 (fraction less than 40 microns) were placed in dry-grinding mill, mixed during 30 minutes, then granulated and burned at different temperatures. Proppants trials with different percentages of CaF_2 were prepared similarly and burned at different temperatures sufficient for complete sintering of the proppants.

Example 4.

20/40 mesh proppants of Malyshevsky deposit sand (79 mass.% - SiO_2, 11 mass.% - Al_2O_3, 8 mass.% - K_2O+N_2O, additives – the rest) and clay (67.5 mass.% - SiO_2, 17.3 mass.% - Al_2O_3, 12.2 mass.% - K_2O+N_2O, additives – the rest) were manufactured in compliance with the present invention as follows: 1 kg of preliminary grinded sand and clay (40 microns) in ratio: 9.5: 0.5, 15 grams (1.5 mass %) of fluozirconate of potassium, and 15 grams (1.5 mass %) of aluminum fluoride of sodium (fraction less than 40 microns) were placed in dry-grinding mill, then mixed during 30 minutes, granulated and burned at different temperatures.

Proppants trials of Ilynsky sand (93 mass.% - SiO_2, 3 mass.% - Al_2O_3, 2 mass.% - K_2O+N_2O, additives – the rest) and of Nikolsky sand (70 mass.% - SiO_2, 12 mass.% - Al_2O_3, 5 mass.% - K_2O+N_2O, additives – the rest) of Sverdlovsky region deposits were prepared similarly.

The following tests of prepared trials were done:

1) crush test at 7500 psi

2) turbidity test of wetting fluid in accordance with standard method of ISO 13503 – 2:2006(E).

The tests results are presented in the Table 1 here below.

Table 1 – properties of siliceous proppant

№	Proppant composition	Temperature of sintering, ^0C	Crush resistance, mass.% at 7500 psi	Turbidity, FTU
1	Proppants of magnesia-silica	1180	5.0	63

	(analog)			
2	Proppant of composite siliceous material (prototype)	1150	4.3	60
3	Proppant of composite siliceous material with 9% of fluozirconate of potassium (fraction less than 40 microns)	950	4.1	58
4	Proppant of magnesia-silica material with 1.2 mass.% of fluorine-apatite (fraction less than 40 microns).	1050	4.7	60
5	Proppant of magnesia-silica material with 10 mass.% of fluorine-apatite (fraction less than 40 microns).	950 -1050	Multiple cakes are formed	-
6	Proppant of magnesia-silica material with 4 mass.% of fluorine-apatite (fraction less than 40 microns).	1040	4.9	61
7	Proppant of Pyshminsky sand and feldspar (9:1) with 5 mass.% of CaF_2	1000	3.8	38
8	Proppant of Pyshminsky sand and feldspar (9:1) with 1 mass.% CaF_2 (fraction less than 40 microns).	1060	4.3 Proppants cakes are formed	-
9	Proppant of Pyshminsky sand and feldspar (9:1) with 10 mass.% of CaF_2 (fraction less than 40 microns).	950 - 1050	Proppants cakes are formed	-
10	Proppant of Pyshminsky sand and feldspar (9:1) with 10 mass.% of CaF_2 (fraction more than 40 microns).	1050	Large quantity of cakes are formed	-
11	Proppant of Malyshevsky sand and clay (9.5 : 0.5) with 1.5 mass.% of fluozirconate of potassium and 1.5 mass.% aluminum fluoride of sodium (fraction more than 40 microns).	980	4.0	32
12	Proppant of Malyshevsky sand and clay (9.5 : 0.5) with 1.5 mass.% of fluozirconate	1000	3.3	34

	of potassium и 1.5 mass.% of aluminum fluoride of sodium (fraction less than 40 microns)			
13	Proppant of Malyshevsky sand and clay (9.5 : 0.5) with 1.5 mass.% of fluozirconate of potassium и 1.5 mass.% of aluminum fluoride of sodium (fraction less than 40 microns)	1020	3.5	30
14	Proppant of Malyshevsky sand and clay (9.5 : 0.5) with 1.5 mass.% of fluozirconate of potassium и 1.5 mass.% of aluminum fluoride of sodium (fraction less than 40 microns)	1060	Proppants cakes are formed	-
15	Proppant of Malyshevsky sand and clay (9.5 : 0.5) with 1.5 mass.% of fluozirconate of potassium и 1.5 mass.% of aluminum fluoride of sodium (fraction more than 40 microns)	1040	5.4 Proppants cakes are formed	56
16	Proppants of Malyshevsky sand and clay (9.5 : 0.5) with 0.4 mass.% of fluozirconate of potassium and 0.4 mass.% of aluminum fluoride of sodium (fraction more than 40 microns)	1050	6.0	58
17	Proppants of Nikolsky sand and clay (9.5 : 0.5) with 1.5 mass.% of fluozirconate of potassium and 1.5 mass.% aluminum fluoride of sodium (fraction less than 40 microns)	950 - 1050	4.3 – 8.0	57 – 60
18	Proppants of Ilynsky sand and clay (9.5 : 0.5) with 1.5 mass.% of fluozirconate of potassium and 1.5 mass.% aluminum fluoride of sodium (fraction less than 40 microns)	950 - 1050	3.3 – 3.7	30 – 34

The analysis of the table data demonstrates that process of the present invention of siliceous proppants manufacture allows to get proppants (samples ## 7, 11-13, 18) having decreased turbidity of wetting fluid and raised mechanical strength obtained by the increase of general quantity of glass phase and its more equal distribution in the volume of proppant granule compared to common analogs.

Proppants manufactured from raw materials containing less than 71 mass % of SiO_2 and without non-organic fluoride (samples ## 1,2,3,17), have decreased mechanical strength and raised turbidity of wetting fluid.

WHAT IS CLAIMED IS:

1. A method for the production of siliceous proppants consisting of SiO_2 71 Wt.% or more, comprising feed preparation by mixing precursor powdered components, its granulation and calcinating, wherein at the stage of preparing feed material ground to the size of 40 μm or less, feed material is additionally introduced with nonorganic fluoride of the same mesh size totaling 1,0-9,0 Wt.%, and calcinating of pellets is performed within the temperature range of 950-1050^0.

2. The method according to claim 1, wherein the ground nonorganic fluoride is taken as a mono-compound as well as a mixture of several non-organic fluoride compounds.