IN THE UNITED STATES DISTRICT COURT
FOR THE NORTHERN DISTRICT OF GEORGIA
ATLANTA DIVISION

C-E Minerals, Inc.,)
)
Plaintiff,)
)
v.) CIVIL ACTION FILE
)
CARBO Ceramics Inc.,) NO.: 1:11-CV-2574-JOF
)
Defendant.)

Declaration of Frank Lowrey

1. My name is Frank Lowrey. I am over the age of 18 and otherwise fit and competent to make this declaration. I make this declaration based on documents on file in government databases maintained by the U.S. Patent and Trademark Office and the Securities and Exchange Commission

Expired Patents Discussing the Use of Andersonville, Georgia Clay to Make Proppants

2. The U.S. Patent and Trademark Office maintains a searchable database of U.S. patents at http://patft.uspto.gov/. Exhibits 1-7 and 9-10 to my declaration are copies of patents maintained on and printed from that database.

U.S. Patent No. 4,921,820

3. U.S. Patent No. 4,921,820 relates to "[a] lightweight oil and gas well proppant" made from "a mixture of kaolin clay." Exhibit 1, p. 1 (Abstract). It was filed in 1989 and issued in 1990 to the assignee Norton-Alcoa Proppants. *Id.* This patent discusses the types of clay, including clay from C-E's Andersonville, Georgia facility, preferred for making proppants:

> The preferred raw materials for use in making the low specific gravity, high strength proppants of the present invention are kaolin clay and amorphous to microcrystalline silica. Preferably the kaolin clay consists largely of kaolinite ($Al_2Si_2O_5(OH)_4$) and is essentially free of sand (i.e., quartz). ***One source of such material is from C.E. Minerals, headquartered in King of Prussia, Pennsylvania. The kaolinite deposits owned by C.E. Minerals are mined at C.E. Mineral's Mulcoa operations in Andersonville, Georgia.*** The Andersonville kaolin deposits owned by C.E. Minerals are well described in a report by Alfred D. Zapp entitled "Bauxite Deposits of the Andersonville District, Georgia", U.S. Geological Survey Bulletin 1199-G. The report is incorporated herein by reference. The report states that the deposit consists largely of the mineral kaolinite and is essentially sand free. The chief impurities are compounds of iron and titanium and small amounts of gibbsite. The kaolin clay is deposited in tabular lenticular masses. Raw materials containing significant amounts of sand (free silica or quartz) produce a weaker proppant, while raw materials containing gibbsite or other hydrated aluminas yield a product having an undesirably high specific gravity.

Id., p. 3, Column 4, lines 10-33 (emphasis added).

4. Patent No. 4,921,820 further explains:

> In general the kaolin clay most useful as a raw material in making the proppants in accordance with the invention may contain by chemical analysis about 45 w/o [*i.e.*, weight-percentage] alumina and 52 w/o silica, less than 1 w/o iron oxide and less than 2 w/o (preferably less than 1 w/o) free quartz. Preferably the kaoline clay approaches 100% kaolinite. Most preferably the amount of free quartz is non-detectable.

Id., p. 3, Column 4, lines 46-53.

5. Patent No. 4,921,820 includes an illustrative example (Example III) involving the use of clay from C-E's Andersonville, Georgia facility to produce proppants:

> In this example a kaolin clay was obtained from C. E. Minerals. This clay was mined at their Mulcoa operation in Andersonville, Georgia. The chemical and mineralogical composition of thE calcined clay is indicated in Tables I and II.

Id., p. 7, Column 11, lines 59-63. The referenced Tables I and II are at pages 5-6 of the patent.

U.S. Patent No. 4,977,116

6. U.S. Patent No. 4,977,116 also relates to "[a] lightweight oil and gas well proppant" made from "a mixture of kaolin clay." Exhibit 2, p. 1 (Abstract). It was filed and issued in 1990 to the assignee Norton-Alcoa. *Id.* It contains substantively the same information regarding the use of clay mined from C-E's

Andersonville, Georgia clay to make proppants as Patent No. 4,921,820, discussed immediately above. *Id.*, p. 3, Column 4, lines 15-68; pp. 5-6 (Tables I and II); p. 7, Column 11, lines 59-63 (Example III).

U.S. Patent No. 5,030,603

7. U.S. Patent No. 5,030,603 also relates to "[a] lightweight oil and gas well proppant" made from "kaolin clay powder." Exhibit 3, p. 1 (Abstract). It was filed in 1990 and issued in 1991 to the assignee Norton-Alcoa. *Id.* This patent explains as follows:

> The preferred raw material for use in making the low specific gravity, high strength proppants of the present invention is kaolin clay. Preferably the kaolin clay consists largely of kaolinite ($Al_2Si_2O_5(OH)_4$) and is essentially free of sand (i.e., quartz). One source of such material is from the American Cyanamid Company ***in Andersonville, Ga.*** The Andersonville kaolin deposits owned by American Cyanamid are well described in a report by Alfred D. Zapp entitled "Bauxite Deposits of the Andersonville District, Ga.", U.S. Geological Survey Bulletin 1199-G. This report is incorporated herein by reference. The report states that the deposit consists largely of the mineral kaolinite and is essentially sand free. The chief impurities are compounds of iron and titanium and small amounts of gibbsite. The kaolin clay is deposited in tabular lenticular masses, the thicker of which may have cores of bauxite or bauxitic clay. Raw materials containing significant amounts of sand (free silica or quartz) produce a weaker proppant, while raw materials containing too much gibbsite or other hydrated aluminas yield a product having an undesirably high specific gravity. ***Another source of material believed to be suitable is the kaolin clay mined at the Mulcoa operations in Andersonville, Ga. of C.E. Minerals, headquartered in King of Prussia, Pa.***

> In general the kaolin clay most useful as a raw material in making the proppants in accordance with the invention may contain by chemical analysis between about 43 w/o to 58 w/o alumina, about 37 w/o to 52 w/o silica, less than 2 w/o (preferably less than 1 w/o) iron oxide and less than 5 w/o free quartz. Preferably, the kaolin clay comprises between 70 w/o and 90 w/o kaolinite, between 5 w/o and 25 w/o cryptocrystalline to amorphous gibbsite and less than 5 w/o other crystalline materials.
>
> Preferably the amount of free quartz is less than 2 w/o and most preferably is non-detectable. Other naturally occurring minerals which may be present in minor or trace amounts include anatase and rutile. Minerals whose presence in the raw material appear to be somewhat detrimental to the properties of the final product include quartz, pyrite, marcasite, siderite, micas and montmorillonites.

Id., p. 3, Column 3, line 58, through Column 4, line 33 (emphasis added).

8. Patent No. 5,030,603 contains several illustrative examples of the patented process, including “Example I,” which employed “milled, calcined kaolin clay obtained from the American Cyanamid, Andersonville, Ga. deposits and having the chemical and mineralogical composition indicated in Tables I and II.” *Id.*, p. 5, Column 8, lines 58-61. The first column of Table I states the proportions of Al_2O_3, SiO_2, Fe_2O_3, TiO_2, CaO, MgO, Na_2O, K_2O in the Andersonville clay employed in Example I to make proppants. *Id.* The first column of Table II contains information about the major and minor minerals contained in that clay. *Id.* at Table II.

U.S. Patent No. 4,921,821

9. U.S. Patent No. 4,921,821 relates to "[a] lightweight oil and gas well proppant" made from "kaolin clay powder." Exhibit 4, p. 1 (Abstract). It was filed in 1989 and issued in 1990 to the assignee Norton-Alcoa Proppants. *Id.* It contains substantively the same information regarding the "preferred raw material" for use in making proppants, including the use of Andersonville, Georgia clay, as contained in Patent No. 5,030,603 discussed immediately above. *Id.*, p. 3, Column 3, line 56, through Column 4, line 30; p. 5 (Example I and Tables I & II).

Expired Patents of CARBO or CARBO Predecessors Discussing the Composition of Raw Materials Used to Make Proppants

U.S. Patent No. 5,120,455

10. U.S. Patent No. 5,120,455 ("Hydraulic Fracturing Propping Agent") was filed in 1990 and issued in 1992 to CARBO Ceramics Inc., as the first-listed assignee. Exhibit 5, p. 1. That patent states:

> For purposes of the present invention the propping agent particles should have an alumina (Al_2O_3) content of between 40 and 60%, preferably between 45.5 and 60%, and a silica (SiO_2) content of between 36.5 and 56.5%, preferably between 36.5 and 51%. ***Good results have been obtained with material having the following composition (calcined basis)***:

SiO_2	45.8
Al_2O_3	50.7
TiO_2	2.60

Fe_2O_3	0.70
CaO	0.03
MgO	0.04
Na_2O	0.06
K_2O	0.05
Li_2O	0.02
Total	100.00

Id., p. 9, Column 3, line 58, through Column 4, line 9 (emphasis added).

11. Patent No. 5,120,455 further explains:

> In a preferred embodiment, the propping agent particles are made from Eufaula bauxite. The term "Eufaula bauxite" refers to a bauxitic-kaolin type material deposited in and around Eufaula, Alabama. See Burst, J. F., "Genetic Relationship of the Andersonville, Georgia and Eufaula, Ala. Bauxitic-Kaolin Areas", Society of Mining Engineers, *AIME Transactions*, Vol. 246, pp. 137-144 (June 1974), which is incorporated by reference herein as background information. Preferably, the Eufaula bauxite will contain at least some (above 5%) gibbsite. The greater the gibbsite content the higher the loss on ignition. Preferably the loss on ignition will be between 14.5 and 20%. Good results have been obtained with a gibbsite content yielding a loss on ignition of about 17.1%.
>
> A small amount (up to 5%) of the Eufaula bauxite may be replaced with a crush strength enhancer selected from the group: nepheline syenite, fused bauxite dust, wollastonite, talc, and feldspar. Of these, nepheline syenite is the preferred crush strength enhancer.

Id., p. 9, Column 4, lines 12-32.

12. Example 11 in Patent No. 5,120,455 "illustrates a method of making the hydraulic fracturing propping agents." *Id.*, p. 12, Column 10, lines 50-52. "The starting material in this example is a bauxitic-kaolin ore from Eufaula, [Ala.]

having the following analysis by weight after ignition at 800 °C.: Al_2O_3 50.7%; SiO_2 45.8%; TiO_2 2.60%; Fe_2O_3 0.71%; with the remainder being alkali and alkali-earth metal oxides." *Id.*, p. 12, Column 10, lines 59-63.

U.S. Patent No. 4,879,181

13. U.S. Patent No. 4,879,181 ("Sintered Spherical Pellets Containing Clay as a Major Component Useful for Gas and Oil Well Proppants") was filed in 1987 and issued in 1989 to the assignee CARBO Ceramics Inc. Exhibit 6, p. 1. The patent explains that proppant pellets may be prepared from a mixture of any of the clays described in Table I with bauxite or alumina or mixtures of these. *Id.*, p. 3, Column 4, lines 45-48. Table I states the chemical composition of each of the clays analyzed in the patent, including the exact proportion of Al_2O_3, SiO_2, Fe_2O_3, TiO_2 and other compounds. *Id.* Table II states the chemical composition, roundness, sphericity, acid solubility, bulk density and crush tolerance for pellets made using various blends of these clays. *Id.*, pp. 5-6.

U.S. Patent No. 4,623,630

14. U.S. Patent No. 4,623,630 was filed in 1983 and issued in 1986 to the assignee Standard Oil Proppants Company. Exhibit 7, p. 1. CARBO's 1997 10-K states that: "CARBO Ceramics was formed in 1987 for the purpose of purchasing the assets of Standard Oil Proppants Company Ltd. (SOPCO). SOPCO was a joint

venture formed to operate the combined proppant businesses of the Carborundrum Company and Dresser Industries." Exhibit 8, p. 2 (excerpts of CARBO's 1997 10-K , as maintained on the S.E.C.'s "Edgar" database, http://www.sec.gov/Archives/edgar/data/1009672/0000950134-98-002057.txt).

15. Patent No. 4,623,630 relates to spherical oil and gas well proppants. Exhibit 7, p. 2, Column 1, lines 14-20. Like the CARBO patent discussed above, this patent explains that "[p]ellets according to the present invention and for use with the present invention may be prepared from a mixture of any of the clays described in Tables I and II with one or more bauxites or alumina or mixtures of these." *Id.*, p. 4, Column 5, lines 23-27. Tables I and II describe the chemical composition, loss on ignition, specific gravity and other characteristics of the clays referenced in the preceding sentence. *Id.*

U.S. Patent No. 4,658,899

16. U.S. Patent No. 4,658,899 was filed in 1985 and issued in 1987 to CARBO's predecessor, Standard Oil Proppants Company. Exhibit 9. It contains the same substantive information regarding clay composition and characteristics as Patent No. 4,623,630, discussed immediately above. *Id.*, p. 4, Column 5, lines 23-27 and Tables I & II.

U.S. Patent No. 4,522,731

17. U.S. Patent No. 4,522,731 ("Hydraulic Fracturing Propping Agent") was filed in 1982 and issued in 1985 to Dresser Industries, Inc. as the assignee. Exhibit 10. As noted above, Dresser Industries was originally a joint venturer in Standard Oil Proppants Company (SOPCO), whose assets were purchased by CARBO in 1987.

18. Patent 4,522,731 explains:

> For purposes of the present invention [spherical proppants] the propping agent particles should have an alumina (Al_2O_3) content of between 40 and 60%, preferably between 45.5 and 60%, and a silica (SiO_2) content of between 36.5 and 56.5%, preferably between 36.5 and 51%. ***Good results have been obtained with material having the following composition (calcined basis)***:

SiO_2	45.8
Al_2O_3	50.7
TiO_2	2.60
Fe_2O_3	0.70
CaO	0.03
MgO	0.04
Na_2O	0.06
K_2O	0.05
Li_2O	0.02
Total	100.00

Id., p. 8 Column 3, line 53, through Column 4, line 4 (emphasis added).

19. Example 11 in Patent 4,522,731 "illustrates a method of making hydraulic fracturing propping agents." *Id.*, p. 11, Column 10, lines 35-37. "The

starting material in this example is a bauxitic-kaolin ore from Eufaula, Ala. having the following analysis by weight after ignition at 800 °C.: Al_2O_3 50.7%; SiO_2 45.8%; TiO_2 2.60%; Fe_2O_3 0.71%; with the remainder being alkali and alkali-earth metal oxides." *Id.*, p. 11, Column 10, lines 43-47.

CARBO Ceramics Inc.'s Mining Agreement with Arcilla Mining and Land Co.

20. Attached as Exhibit 11 are excerpts printed from CARBO Ceramics Inc.'s Form 2002 10-K filing, as it appears on the S.E.C.'s "Edgar" database. www.sec.gov/Archives/edgar/data/1009672/000095013403003746/d03686e10vk.txt.

21. CARBO's 2002 10-K reflects that CARBO produces ceramic proppants from (among other places) a production facility in McIntyre, Georgia, which is in Wilkinson County, Georgia. *Id.*, p. 5.

22. Attached to my declaration as Exhibit 12 is a copy of a "Mining Agreement" between a Georgia company (Arcilla Mining & Land Co.) and CARBO dated as of January 1, 2003. As reflected on the face of this exhibit, CARBO filed this Mining Agreement as Exhibit 10.8 to its 2002 10-K, and it is publicly available on the Edgar database cited above.

23. This Mining Agreement "set[s] out the terms pursuant to which [Arcilla] shall mine (either from lands owned or leased by [CARBO] … or from lands owned or leased by [Arcilla] … and deliver to [CARBO's] Wilkinson County, Georgia manufacturing plant a supply of kaolin, a naturally occurring mineral more particularly described (and meeting the specifications set forth) in Exhibit A [to the Mining Agreement]…." *Id.*, p. 1.

24. The Mining Agreement states that its term "shall be 20 years commencing January 1, 2003, and ending December 31, 2022." *Id.* § 1.

I declare under penalty of perjury and subject to 28 U.S.C. § 1746 that the foregoing is true and correct.

Executed on October 31st, 2011.

Frank Lowrey

EXHIBIT 1

United States Patent [19]
Rumpf et al.

[11] **Patent Number: 4,921,820**
[45] **Date of Patent: May 1, 1990**

[54] LIGHTWEIGHT PROPPANT FOR OIL AND GAS WELLS AND METHODS FOR MAKING AND USING SAME

[75] Inventors: **David S. Rumpf; Paul R. Lemieux,** both of Ft. Smith, Ark.

[73] Assignee: **Norton-Alcoa Proppants,** Fort Smith, Ark.

[21] Appl. No.: **297,876**

[22] Filed: **Jan. 17, 1989**

[51] **Int. Cl.**^{5} **C04B 35/10**
[52] **U.S. Cl.** **501/128;** 501/127; 501/133; 501/144; 166/280
[58] **Field of Search** 501/133, 144, 127, 128; 166/280

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,642,505	2/1972	Bakker .	
4,440,866	3/1984	Lunghofer et al.	501/127
4,623,630	11/1986	Fitzgibbon	501/141
4,632,876	12/1986	Laird et al.	428/404
4,639,427	1/1987	Khaund	501/128
4,658,899	4/1987	Fitzgibbon	166/280
4,668,645	5/1987	Khaund	501/127
4,680,230	7/1987	Gibb et al.	428/403
4,713,203	12/1987	Andrews	264/117

Primary Examiner—Mark L. Bell
Assistant Examiner—Karl Group
Attorney, Agent, or Firm—Weil, Gotshal & Manges

[57] **ABSTRACT**

A lightweight oil and gas well proppant made by simultaneously mixing and compacting a mixture of kaolin clay which has been calcined at a temperature low enough to prevent the formation of mullite and crystobalites to an LOI of 12 or less when tested at 1400° C., and amorphous to microcrystalline silica both of which have been milled to an average agglomerated particle size of 7 microns or less to form green pellets, and then drying, screening, and sintering the pellets to form proppant pellets having a specific gravity of 2.7 or less, the proppant having a conductivity of at least 3,000 millidarci-feet as measured by the Stim-Lab Technique after 50 hours at 8,000 psi and 275° F. in the presence of deoxygenated aqueous 2% solution of KCl using sandstone shims.

21 Claims, No Drawings

LIGHTWEIGHT PROPPANT FOR OIL AND GAS WELLS AND METHODS FOR MAKING AND USING SAME

FIELD OF INVENTION

This invention relates generally to lightweight proppants for oil and gas wells and more particularly to lightweight proppants for oil and gas wells which are lighter in weight than existing lightweight proppants but which have strength and conductivity similar to and preferably substantially higher than such existing lightweight proppants, and to methods of making and using such proppants.

BACKGROUND

Hydraulic fracturing is a process of injecting fluids into a selected oil or gas bearing subsurface earth formation traversed by a well bore at sufficiently high rates and pressures such that the formation fails in tension and fractures to accept the fluid. In order to hold the fracture open once the fracturing pressure is released a propping agent (proppant) is mixed with the fluid which is injected into the formation.

Hydraulic fracturing increases the flow of fluids from an oil or gas reservoir to a well bore in at least three ways: (1) the overall reservoir area in communication with the well bore is increased, (2) the proppant in the fracture generally has significantly higher permeability than that of the formation, thereby allowing fluids to flow more easily, and (3) the high conductivity channel causes large pressure gradients to be created in the reservoir past the tip of the fracture.

Proppants are generally strong, preferably substantially spherical, particulates that should be able to withstand the high temperatures and pressures and corrosive environments experienced in the subsurface formations surrounding an oil or gas well. Early proppants were formed of material such as glass beads, sand, walnut shells and aluminum pellets. These materials did not have sufficient strength or resistance to corrosion to be successful in many wells, particularly where closure pressures above a few thousand psi were experienced.

U.S. Pat. No. 4,068,718 to Cooke relates to a proppant which Cooke states is formed of "sintered bauxite" that has a specific gravity greater than 3.4. Cooke states that specific gravities above 3.4 are required in order that the proppant have sufficient compressive strength to resist fragmentation under the high stress levels experienced in use. While the proppant described in Cooke's example proved to have sufficient strength to resist crushing, the high specific gravity was undesirable since it required the use of higher viscosity fracturing fluids and resulted in a lower volumetric proppant concentration for a given weight of proppant loading in a fracturing fluid when compared with that achieved by a proppant of lower specific gravity. In general, the higher the volumetric concentration of the proppant in the fracturing fluid, the wider the propped fracture will be after the fracturing pressure is released.

U.S. Pat. No. 4,427,068 to Fitzgibbon relates to intermediate strength composite proppants made by mixing calcined diaspore clay, burley clay or flint clay with alumina, "bauxite" or mixtures thereof such that the ratio of alumina to silica in the composite mix is between nine to one and one to one. The powdered starting materials are mixed in an Eirich mixer and while the mixing is in progress sufficient water is added to cause

formation of composite spherical pellets from the powdered mixture. Fitzgibbon states that the rate of water addition is not critical. The pellets are dried and then furnaced to sinter the pellets. The sintered pellets have a specific gravity of between 2.7 and 3.4.

U.S. Pat. No. 4,522,731 to Lunghofer relates to an intermediate strength proppant having an alumina content between 40% and 60% which is produced using a spray agglomeration process and which has a density of less than 3.0 gr/cc. In a preferred embodiment Lunghofer produces his proppants from "Eufaula bauxite" which it states is bauxitickaolin type material deposited in and around Eufaula, Alabama. According to Lunghofer, the Eufaula bauxite preferably contains at least some (above 5%) gibbsite.

U.S. Pat. No. 4,668,645 to Khaund relates to an intermediate strength proppant made from a mined "bauxitic clay" having a specified chemical composition.

The proppants described in the Fitzgibbons, Lunghofer and Khaund patents have specific gravities lower than that of the earlier Cooke proppant and proppants having such lower specific gravities have been used with some success in intermediate depth wells where the stress on the proppant is in the 5,000 to 10,000 psi range. It will be desirable, however, to have still lighter weight proppants which are easier to transport in the fracturing fluid and are therefore carried farther into the fracture before settling out and which will yield a wider propped fracture than the known lower specific gravity proppants. The lighter weight proppant should, however, have a conductivity rating at least as high as and preferably substantially higher than those obtainable with the presently available "lightweight" proppants.

The conductivity of a proppant under specific conditions of stress, temperature, corrosive environment and time is the single most important measure of its quality. The conductivity of a packed proppant such as might be deposited in a fracture is defined as the permeability of the proppant pack multiplied by the width of the propped fracture and is usually stated in units of millidarci-feet ("md-ft").

The conductivity of currently available intermediate strength proppants is frequently measured by the tentative API 8 hour procedure, "Tentative Fifth Draft of REcommended Practices For Evaluating Short Term Proppant Pack Conductivity", (March 1987) (hereinafter the "API 8 hour Procedure"), which procedure is hereby incorporated by reference.

Recently a consortium of some twenty-eight organizations involved in various aspects of the fracturing and stimulation business has sponsored research on ways of evaluating and improving stimulation techniques. Stim-Lab, Inc. of Duncan, OK acts as the testing arm of the consortium to develop consistent and repeatable testing procedures for proppants including tests for determining their permeability and conductivity. The long term conductivity testing techniques developed by Stim-Lab have been widely accepted in the industry and are described in a publication of the Society of Petroleum Engineers, No. SPE 16900, entitled "An Evaluation of the Effects of Environmental Conditions and Fracturing Fluids on the Long-Term Conductivity of Proppants" by G. S. Penny of Stim-Lab, Inc., which publication is hereby incorporated by reference. It should be understood that any gap in the description in the SPE publication should be filled in by reference to the API 8 hour Procedure. The testing techniques used by the applicants to determine the conductivity of the proppants of the present invention as they are intended to be supplied to a customer (referred to as the "Stim-Lab Technique") are essentially identical to those described in SPE publication No. 16900 using Model-K 500 or sandstone shims in the conductivity cells, as noted herein. A single cell was used rather than stacking 4 cells in the manner described in the SPE publication. This however should have no effect on the measured results. The Stim-Lab Technique is considered to yield conductivity measurements that are repeatable to within about 5–10%.

SUMMARY OF THE INVENTION

In accordance with the invention there is provided a low density, high strength proppant which is formed of solid ceramic particles having a dry specific gravity less than 2.70 and preferably 2.60 or less and a conductivity of at least about 3,000 md-ft and preferably at least 4000 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of a deoxygenated 2% aqueous solution of KCl as measured by the Stim-Lab Technique using sandstone shims. Most preferably the conductivity is at least 4400 md-ft as measured under the above conditions.

The proppant of the invention may be produced by milling calcined kaolin clay and an amorphous to microcrystalline silica to an average particle size of less that 7 microns, and preferably about 3.0 microns or less and pelletizing a mixture of the resulting powders in a compacting mixer. Preferably the mixture contains between 55 weight percent ("w/o") and 90 w/o kaolinite and between 45 w/o and 10 w/o silica, although the percentages may fall outside these ranges. Kaolinite is normally the major component of the mixture. However, in the limit the silica content could reach 100% yielding a proppant of essentially all crystobablite baving a specific gravity of about 2.33. The kaolinite and silica are preferably milled together.

The kaolin clay is calcined at a temperature of less than 900° C. to reduce the loss on ignition ("LOI") to 12 w/o or less when tested at 1400° C., and preferably to about 2 w/o LOI when tested at 1400° C. It is important that the calcining be done at a low enough temperature that the kaolin clay does not undergo a phase transformation to mullite and crystobalite. The silica should not contain any significant amount of crystalline quartz, other than amorphous to microcrystalline quartz as hereinafter defined, and is preferably dried to a LOI of about 1 w/o when tested at 1000° C.

Preferably, an organic binder is first dispersed in the milled material in the mixer and then water is added to the powder at a controlled rate while mixing and compacting the powder to form rough pellets of a desired size. Next, with the mixer still running, additional dry, milled material is slowly added to yield smooth, spherical pellets. The pellets are then dried and fired to convert the material to proppant pellets that preferably comprise between about 35 (w/o) and 60 w/o mullite, between about 35 w/o and 60 w/o crystobalite and a minor amount (less than 10 w/o) of a glassy phase. The proppant has a specific gravity of less than 2.70 and preferably of 2.60 or less. Most preferably the pellets comprise between 35 w/o and 50 w/o mullite and 50 w/o to 60 w/o crystobalite.

In accordance with another aspect of the invention, the proppant is mixed with a fluid and injected into a subterranean formation under high pressure to open a fracture, with the proppant remaining in the fracture to prop it open after the fracturing pressure is removed. The measured conductivity of the proppants of the present invention are equal to and usually substantially better than those of other known lightweight proppants which have higher specific gravities and higher weight per unit of volume.

DETAILED DESCRIPTION

The preferred raw materials for use in making the low specific gravity, high strength proppants of the present invention are kaolin clay and amorphous to microcrystalline silica. Preferably the kaolin clay consists largely of kaolinite ($Al_2Si_2O_5(OH)_4$) and is essentially free of sand (i.e., quartz). One source of such material is from C. E. Minerals, headquartered in King of Prussia, Pennsylvania. The kaolinite deposits owned by C. E. Minerals are mined at C. E. Mineral's Mulcoa operations in Andersonville, Georgia. The Andersonville kaolin deposits owned by C. E. Minerals are well described in a report by Alfred D. Zapp entitled "Bauxite Deposits of the Andersonville District, Georgia", U.S. Geological Survey Bulletin 1199-G. This report is incorporated herein by reference. The report states that the deposit consists largely of the mineral kaolinite and is essentially sand free. The chief impurities are compounds of iron and titanium and small amounts of gibbsite. The kaolin clay is deposited in tabular lenticular masses. Raw materials containing significant amounts of sand (free silica or quartz) produce a weaker proppant, while raw materials containing gibbsite or other hydrated aluminas yield a product having an undesirably high specific gravity.

By amorphous to microcrystalline silica is meant silica which is truly amorphous or is "amorphous" in the sense that the ultimate submicron particles, as seen with the aid of a scanning electron microscope, do not have the angular shape of crystals. One source of amorphous to microcrystalline silica is from Illinois Minerals Company in Cairo, Illinois. This silica, as described by Illinois Minerals, is an extremely fine-grained microcrystalline silica formed by weathering of silica-rich limestone. Materials from other deposits of kaolinite and of amorphous to microcrystalline silica can also be used in making the proppants of the present invention.

In general the kaolin clay most useful as a raw material in making the proppants in accordance with the invention may contain by chemical analysis about 45 w/o alumina and 52 w/o silica, less than 1 w/o iron oxide and less than 2 w/o (preferably less than 1 w/o) free quartz. Preferably the kaoline clay approaches 100% kaolinite. Most preferably the amount of free quartz is non-detectable.

Other naturally occurring minerals which may be present in minor or trace amounts include anatase and rutile. Minerals whose presence in the raw material appear to be somewhat detrimental to the properties of the final product include quartz, pyrite, marcasite, siderite, micas and montmorillonites. The amorphous to microcystalline silica most useful as a raw material in making the proppants in accordance with the invention should contain by chemical analysis at least 94 w/o (preferably 100 w/o) silica.

The kaolin clay is preferably calcined before further processing in order to remove water and organics. In accordance with the invention, applicants have found that the calcining should be performed at a temperature low enough that the kaolin clay does not undergo a phase change to form mullite or crystobalite. Applicants have found that the presence of any significant amount of mullite or crystobalite in the kaolin clay before the final drying and firing steps has a severely detrimental effect on the properties of the proppants produced. Therefore the calcining should be performed at a temperature below 900° C. for a sufficient time that the loss on ignition ("LOI") of the kaolinite is 12 w/o or less and preferably 2 w/o or less when tested at 1400° C. The calcining may be performed relatively quickly at temperatures on the order of 700° to 800° C. or may be performed more slowly at lower temperatures. If the calcining temperature is above about 450° to 500° C., the kaolinite is converted to amorphous alumina and silica (sometimes referred to as "meta kaolinite"). Such a transformation, however, has no adverse effect on the product of the invention and such transformed material will still be referred to herein as kaolinite. The silica should be dried after mining to an LOI of less than 1 w/o when tested at 1,000° C. This drying is typically done at temperatures of between about 150° and 200° C.

The calcined material and the silica is then reduced in particle size, preferably by dry ball milling them in a closed loop system containing a particle classifier. The average agglomerated particle size in this milled material is less than 7 microns and preferably about 3.0 microns or less as measured by a Sedigraph (Micro Meritics Instrument Corp.) or a Granulometer' (Cilas Compagnie Industrielle des Lasars). The true ultimate particle size, however, of the milled raw material (both the kaolin and silica) is much finer than 3.0 microns and is believed to be made up of submicron flakes or particles. Such submicron flakes or particles tend to agglomerate to form the composite particles which are sensed by the measuring instruments. The calcined kaolin clay and silica are mixed together and preferable are milled together. The mixture preferably contains between 55 w/o and 90 w/o kaolinite and between 45 w/o and 10 w/o silica, although different percentage mixtures may be used. Kaolinite is normally the major component of the mixture. However, in the limit the amorphous to microcrystalline silica content can reach 100%, yielding a proppant that is essentially entirely crystobalite having a specific gravity of about 2.33. Such a super lightweight proppant would be very useful in shallow wells when closure stresses are on the order of 4000 psi or less.

The milled raw material is pelletized preferably in a compacting mixer. The preferred commercially available machines for this purpose are the Eirich Countercurrent Intensive Mixers which are manufactured in several sizes of different capacities by the Maschinenfabrik Gustav Eirich of Hardheim, West Germany and distributed in the United States by Eirich Machines, Inc., New York, N.Y.

The Eirich mixer has a rotating mixing pan forming the bottom of the mixing chamber which pan can be either horizontal or inclined at an angle and a "mixing star" which rotates in the opposite direction from the pan. The mixing star rotates about an axis parallel to and offset from that of the pan and has a diameter of about 20 to 25 percent of that of the pan. The preferred form of mixing star for the pelletizing operation is referred to by Eirich as a suction type rotor and has a plurality of vertically extending trapidzoidally shaped mixing elements which extend from the periphery of the rotating element. For the Model R7 machine, the pan has a single rotational speed of about 45 rpm, while the mixing star has a low and a high speed. The low speed is about 700 rpm and the high speed is about twice that, about 1400 rpm. The rotational speeds of the elements of the larger mixers are adjusted so that rotating elements have similar tip speeds. The mixer may also contain a second mixing star upon which can be mounted plows for cleaning the sides of the rotating pan. This second mixing star is also mounted eccentrically in the mixer and rotates in the opposite direction from the mixing pan. An example of another compacting mixer that is believed suitable for use in the present invention is the Littleford Lodige mixer.

The milled powder charge is preferably first mixed dry in the mixer with up to about 3 w/o (calculated on the basis of the initial milled powder charge) of an organic binder such as gelatinized cornstarch for a period of about 30 seconds with the suction rotor on the low speed setting in order to fully disperse the binder in the raw material powder.

It is preferred that such binders be such that they are pyrolized or driven off during later firing of the proppant pellets. The amount of the binder is normally on the order of 1 w/o to 3 w/o of the initial milled powder charge. It is possible to make pellets with the method of the invention without a binder but it is believed that the use of a binder results in improved properties and yield.

Next water is added at a controlled rate to the mixer with the suction rotor running at the low speed setting to initially pelletize the material. The rate of water addition should be controlled properly to facilitate the formation of the pellets in the mixer and can affect the quality of the final product. Typically the total amount of water for the Model R7 Eirich mixer is from about 35 to 55 w/o of the initial starting material and preferably about 43 to 50 w/o. Preferably between about 40 and 60 w/o of the expected total amount of water is added after the binder is dispersed and mixed for about 2 to 4 minutes. Thereafter additions of about 8 to 10% of the total water are made about every 0.75 to 1.5 minutes until irregularly shaped pellets ranging in size from about 1/16 to ⅛ inch in diameter are formed.

Once pellets have formed in the mixer, which at this point are normally large and irregularly shaped, the suction rotor is switched to the high speed setting and additional milled calcined raw material (referred to as "dust") is slowly added to the mixer over a period of about 5 to 7 minutes in order to cause the pellets to become smaller, well shaped spheres of a narrower size distribution, typically 0.02 inches to 0.047 inches. Typically, the amount of dust required to form the desired size spheres is about 42 to 70 w/o of the starting raw material. Preferably about 46 to 54 w/o dust is added.

In some cases the suction rotor is switched back to the low speed setting for a later portion of the 5 to 7 minute period after a major portion of the dust has been added to the mixer. After adding the dust, the suction rotor is then preferably set back to the low speed setting if it has not already been and the mixer run for a further period of about 30 seconds in order to improve the sphericity of the pellets and to increase yield of the desired size range.

The amount and rate of water and dust additions to the mixer can have a significant impact on the conductivity of the proppant produced by the method of the invention. If too much water is added, the particles are poorly shaped and are too large. If the dust is added too quickly it results in a poor yield of particles in the desired size range. If not enough dust is added the particles are poorly shaped and will stick together in agglomerated masses. If too much dust is added the particles have a rough surface and unconsolidated dust remains in the mixer. When the right amount of dust is added, the process yields smooth, spherical, well compacted pellets.

The spherical pellets are next discharged from the mixer and dried to a free moisture content of less than 10% and preferably less than 5%. The drying temperature and time does not appear to be critical and it has been found, for instance, that drying at temperatures of 150° C. overnight, or of 260° C. for 10 to 15 minutes are suitable. Once dried, the desired size spherical pellets are separated by screening for instance to a 18/35 mesh size. The larger than 18 mesh and finer than 35 mesh are recycled to be repelletized. The screened particles in the desired size range are then sintered, for instance in a rotary kiln, at a temperature between 1300° and 1500° C., preferably between 1375° to 1425° C. for about 15 to 30 minutes at temperature. The total time in the kiln is normally from about 1 to 1½ hours. The particles shrink upon firing by about 15% to 20%. The desired finished size is typically between about 0.0167 inches and 0.0331 inches but can be larger or smaller as needed. The particular temperature to which the screened particles are fired is selected in order to maximize their strength. This temperature depends on several variables, some of which are the raw material mineralogy, the milled particle size, the pellet size and the volume of material in the kiln.

After firing, the pellets are again screened to the desired final size. A typical product size is 20/40 mesh which contains 90 w/o of its pellets of between 0.0167 inches and 0.0331 inches in size and preferably 90 w/o of the pellets between about 0.0232 inches and 0.0331 inches in size.

The proppants of the invention have been found to have surprisingly and unexpectedly high conductivities for having such low specific gravities. More particularly, the conductivities of the proppants of the preferred embodiment of the present invention are at least 3000 md-ft and preferably at least 4000 md-ft after 50 hours at 8000 psi and 275° F. in the presence of a deoxygenated 2% aqueous solution of KCl as measured by the Stim-Lab Technique using sandstone shims. Most preferably the conductivity is at least 4500 md-ft when measured under the above conditions. The proppants of the present invention have specific gravities of less than 2.70, and preferably 2.60 or less, which are lower than those of other commercially available lightweight proppants. In fact, the preferred proppants of the present invention are even lighter than sand (specific gravity 2.64), the lightest proppant which has heretofore been in common commercial use. The conductivity of the proppants of the present invention are between about 3 and 20 times that of sand, however, depending upon operating conditions. Sand is of little use at pressures on the order of 8000 psi while the preferred proppants of the present invention still have high conductivities, on the order of as much as 4500 md-ft, at such pressures.

Compared to another heavier commercially available proppant which is considered to be in the lightweight range, the preferred proppants of the present invention have substantially higher conductivities. The commercially available "lightweight" proppant has been measured in accordance with the Stim-Lab technique to have a conductivity of 6067 md-ft after 50 hours at 250° F. and 6000 psi closure stress in the presence of deoxygenated aqueous 2% KCl solution using sandstone shims. A proppant in accordance with the preferred embodiment of the present invention had conductivity values of 7855 md-ft when measured under the same conditions. The same commercially available "lightweight" proppant had conductivities measured by the Stim-Lab technique of 3616 to 3700 md-ft after 50 hours at 275° F. and 8000 psi while the proppant of the present invention had a conductivity of 4459 md-ft under similar conditions.

The Loose Pack Bulk Density (LPBD) of the proppant of the invention used in the above example is 1.45 gms/cm^3. The LPBD of the commercially available "lightweight" proppant used for comparison in the above example is 1.61 gm/cm^3. Their specific gravities were 2.56 and 2.70 respectively.

From a mineralogical point of view the sintered pellets of the present invention are preferably between about 35 w/o and 60 w/o mullite and between about 35 w/o and 60 w/o crystobalite and a minor amount (less than 10 w/o) of a glassy phase. It is believed that the glassy phase is best minimized for the highest quality product.

EXAMPLES

The invention is further illustrated by reference to the following non-limiting examples wherein all percentages are by weight unless otherwise specified. When applicable calcining conditions and milling techniques for each raw material are given with each example. Unless otherwise indicated, the pellets are screened to an 18/35 mesh size after drying and to a 20/30 mesh size after sintering wherein 90% of the pellets are between about 0.0232 inches and 0.0331 inches in size. The typical yield of properly size pellets in the first screening is about 70%. The chemical compositions of the raw materials used in the following examples are summarized in Table I. The mineralogical composition of the calcined kaolin clays as measured by the X-ray diffraction technique is summarized in Table II. The kaolinite in both the Huber 40-C clay and the Mulcoa clay have been transformed to amorphous alumina and silica by being calcined at 750° C. and thus are not detected by X-ray diffraction. The figures in Tables II for the ACCO clay are for the uncalcined material so that kaolinite is detected. Mineralogically the silicas used in the examples is of such a fine grain size as to be virtually undetectable as measured by X-ray diffraction techniques. The components in Table II are divided into major minerals which comprise about 95 w/o of the detected minerals present and the minor minerals which together make up less then 5 w/o of the detected minerals present. Kaolinite is approximately 45 w/o Al_2O_3. After calcining or drying all the raw materials are milled to an average particle size of about 3 microns as measured by a Granulometer. About 90% of the particles were measured to be less than 10 microns in size.

TABLE I

	Example			
	1 Huber 40-C Clay	2 ACCO Clay	3 Mulcoa Clay	4 (Silica)
Chemistry				
Al_2O_3	45.0	45.9	43.7	0.7
SiO_2	53.0	51.4	51.8	99.0
TiO_2	1.8	1.8	1.7	0.5

TABLE I-continued

	Example			
	1 Huber 40-C Clay	2 ACCO Clay	3 Mulcoa Clay	4 (Silica)
Fe_2O_3	0.2	0.9	0.8	0.5

TABLE II

	Example		
Mineralogy	1	2	3
Major Minerals			
Kaolinite	ND	Major	ND
Minor Minerals			
Anatase	Major	Major	Trace
Rutile	ND	Trace	ND
Quartz	ND	ND	Trace
Mullite	ND	ND	ND
Amorphous	Yes	No	Yes

Where "ND" means non-detectable

EXAMPLE I

One hundred (100) lbs. of a kaolin clay/silica mixture was produced by combining 86 lbs. of calcined Huber 40-C kaolin clay (manufactured by the J. M. Huber Corporation) and 14 lbs of dried Imsil A-108 microcrystalline silica (manufactured by Illinois Minerals Company) in an Eirich Model R-7 Compacting Mixer and mixing the two ingredients together for 60 seconds. Both the calcined kaolin clay and the silica had been milled separately to an average particle size of 3 microns as measured by a Granulometer. Hereafter in this example this mixture will be referred to as "blended material".

A 50 lbs. charge of blended material was placed in an Eirich Compacting Mixer having an inclined pan and a suction type rotor along with 1½ lbs. of gelatinized cornstarch binder and mixed for 30 seconds with the suction rotor in its low speed setting in order to fully disperse the binder in the blended material. With the suction rotor rotating at its low speed setting, 9 lbs. of water was added to the mixer and mixed for a period of two minutes. As the suction rotor continued to operate in the low speed setting, seven 2 lb. additions, followed by a 1 lb. addition and then a ½ lb. addition of water were added sequentially to the mixer with a 45 second mixing period after each addition. At this point irregularly shaped pellets had formed.

The rotor was then switched to the high speed setting and an additional 17 lbs. of the same blended material was slowly added to the mixer over a three minute period. Then the rotor was reset to its low speed setting and additional 11 lbs. of the blender material was added over a period of two minutes. The mixing was continued with the suction rotor in the low speed setting for an additional period of 30 seconds. At this point the particles had fairly good sphericity but had rather rough surfaces. An additional 7 lbs. of the blended material was slowly added to the mixer over a 1 minute period and the material mixed for an additional 30 seconds with the suction rotor continuing in the low speed setting. The pellets now had a good spherical shape and smooth surfaces. The pellets were discharged from the mixer and dried overnight at 150° C. in a box oven. After drying the pellets were screened to an 18/35 mesh and fired at 1405° C. in a rotary kiln for a period of about 30 minutes at temperature with a total time in the kiln of approximately 1 hour 15 minutes. After cooling the pellets were screened to a 20/30 mesh. The dry specific gravity of the material was 2.56 as measured by a Beckman air comparison pycnometer Model 930.

A conductivity test using the Stim-Lab Technique referred to above was conducted with final closure stress of 6,000 psi at 250° F. in the presence a deoxygenated aqueous 2% solution of KCl for 50 hours. In accordance with this procedure 63.06 grams of the screened proppant pellets were loaded into a API Hasteloy-C 10 in^2 linear flow cell to give a loading of 2 $lbs./ft^2$ of proppant and leveled loosely with a universal bevel blade device. A ⅜ inch thick sandstone core was placed on top of the test pack followed by an O ring fitted to a piston which was lightly coated with vacuum grease. The loaded test cell was then placed in a 150 ton Dake press and the closure stress was increased to 500 psi at a rate of 100 psi/min. The cell was saturated with deoxygenated aqueous 2 w/o KCl solution and then purged of air at the ambient laboratory temperature of 70° F. to 80° F. A Validyne DP15-30 differential pressure transducer connected across the cell was calibrated with water columns to 0.0001 psi accuracy. Closure stress was then raised to 1,000 psi at a rate of 100 psi/min. A Reservoir Accumulator, made up of two 5 gal and two 1 gal nitrogen driven fluid reservoir accumulators which were filled with a 2 w/o KCl aqueous solution that had been deoxygenated with nitrogen to a level of less than 15 ppb and preferably less than 5 ppb of oxygen was connected to the test cell and set at a driving pressure of 400 psi. The connection of the Reservoir Accumulator to the cell is make through two 150 ml sample cylinders filled with 100 mesh Oklahoma #1 sand with ceramic band heaters in order to saturate the test fluid with silica. It should be noted that the closure stresses on the proppant pack in the cell are stated in terms of the net closure stress on the pack which is equal to the gross pressure applied by the press minus the 400 psi pressure applied by the reservoir accumulator.

The system was allowed 30 minutes to come to equilibrium and a series of five conductivity measurements were taken and averaged. The conductivity was calculated from the darci relationship:

$$k_{wf}=26.78\ \mu Q/P$$

where

k_{wf} = Conductivity (md-ft)

26.78 = factor to account for a 1½×5 inch flow area and pressure in psi

μ = Viscosity of flowing fluid at temperature (cp)

Q = Flow rate (ml/min)

P = Pressure differential across 5 inch flow path.

After the readings were taken at ambient temperature, the temperature was increased to 250° F. and held for 8 hours for temperature uniformity. Next readings with the system at 250° F. were taken at 1,000 psi, 2,000 psi, 4,000 psi and 6,000 psi with the closure stress being raised between levels at a rate of 100 psi/min. After reaching each of the 1,000, 2,000, 4,000 and 6,000 closure stress levels, the system was held at 250° F. for 1.5 hours before the conductivity readings were taken. At the 6,000 psi level the cell was held at 250° F. for 50 hours during which conductivity measurements were taken at 10 hour intervals. The measured conductivity at the 50 hour time was 7,351 md-ft and 7084 md-ft on a second sample of the raw material run at the same time.

EXAMPLE II

In this example a kaolin clay was obtained from the American Cyanamid Co., Andersonville, Georgia. The chemical and mineralogical composition of the uncalcined clay as indicated in Table I and II. This kaolin clay was calcined a 480° C. for approximately 24 hours then crushed to less than ⅛". The crushed kaolin clay was combined with 250 grade air-floated microcrystalline silica provided by the Illinois Minerals Company. This mixture contains 75 w/o clay and 25 w/o silica and hereafter will be referred to as "blended material" in this example. The mixture was tumbled in a "V" blender for approximately 2 minutes to insure complete mixing.

The blended material was next reduced in particle size using a jet mill manufactured by the Fluid Energy Processing Equipment Company of Hatfield, Pennsylvania. The average particle size of this milled material was 3.68 micons as measured by the Leads and Northrup Microtrac II particle size analyzer.

A 45 lb. charge of this blended material was placed in the Eirich Model R-7 Compacting Mixer describved in Example I along with 1½ lbs. of constarch binder and mixed dry for 30 seconds at the low speed setting. Water was then added to the mixer with the mixer operating at the low speed setting with 9 lbs. being added and mixed for 2 minutes followed by 4 additions of 2 lbs. each, one addition of 1 lb. and three additions of ½ lb., with a 45 second mixing period after each addition.

The mixer was then set to the high speed mode and 10 lbs. of the blended material was slowly added to the mixer over a minute period. The mixer was then switched back to the low speed setting and an additional 7 lbs. of the blended material was slowly added over a 2 minute period, followed by a 30 second low speed mixing. An additional 3 lbs. of the blended material was added over the following minute followed by an additional 30 second mixing period at the low speed. Then a final 3 lbs. of the blended material was added over the following minute followed by an additional 30 second mixing period at low speed. The particles were thereafter discharged from the mixer and screened, dried and fired in the same manner as described in Example I with the exception that the sintering temperature was 1395° C. After cooling the pellets were screened to a 20–30 mesh size. The dry specific gravity of the material was 2.52. The Stim-Lab conductivity test described in connection with Example I was then performed except that the readings at the elevated temperature where taken at 275° C. and the maximum stress was 8000 psi. The test yielded a measured conductivity after 50 hours at 8,000 psi and 275° F. of 3,351 md/ft.

EXAMPLE III

In this example a kaolin clay was obtained from C. E. Minerals. This clay was mined at their Mulcoa operation in Andersonville, Georgia. The chemical and mineralogical composition of the calcined clay is indicated in Tables I and II. For this example the clay was calcined in a rotary kiln at 750° C. and held at that temperature for 2 hours. This clay was next crushed to minus ⅛ inch then milled in a similar method as the material in Example II. The average particle size of the milled clay in this example was 3.01 microns as measured by the Leads and Northrup Microtrac II. This milled clay was then mixed with Imseil A-108 silica in a similar manner as in Example I, the ratio again being 86% clay and 14% silica. Again as in the previous examples this mixture will be referred to as "blended material" hereafter in this example.

A 45 lbs. charge of this blended material was placed in the Eirich Model R-7 Compacting mixer described in Example I along with 1½ lbs. of cornstarch binder and mixed with water in the same manner as described in Example I with the exception of adding 2 lb. additions to 17 lb. then 1 lb. additions to 21 lbs. then a ½ lb. addition.

Next 13 lbs. of blended material was slowly added over a minute period with the mixer in the high speed setting. Next the mixer was switched back to the low speed setting and an additional 8 lbs. of blended material was added over a period of 2 minutes after which the mixer continued to be operated for an additional 30 seconds mixing time. The pellets formed by this procedure were slightly wet but had a good spherical shape. The pellets were then removed from the mixer and dried, screened (both before and after sintering) and sintered in the same sintering temperature used was 1,385° C.

The Stim-Lab conductivity test described in Example II was then performed on the proppant resulting in a conductivity measurement of 4,459 md-ft. after 50 hours at 8,000 psi at 275° F. The dry specific gravity of the proppant was 2.59.

In accordance with the method of the present invention the low density high strength proppant particles of the present invention may be injected into fractures in subsurface formation as a propping agent. In fracturing treatment a viscous fluid, often referred to as a "pad" is injected into the well at extremely high pressure to cause the formation to fail in tension and fracture to accept the fluid. The fracturing fluid may be an oil base, water base, acid, emulsion, foam or other fluid. Normally the fluid contains several additives such as viscosity builders, drag reducers, fluid loss additives, corrosion inhibitors, cross linkers and the like. The fluid of the pad is injected until a fracture of sufficient geometry is obtained to permit the placement of the proppant pellets. Normally the treatment is designed to provide a fracture at the well bore of at least 2½ times the diameter of the largest proppant pellet. Once a fracture of the desired geommetry is obtained, the proppants are carried suspended in the fluid pad and placed in the fracture. Following placement of the proppant, the well is shut-in for a length of time sufficient to permit the pressure to bleed off into the formation which in turn causes the fracture to close and exert closure stress on the proppant particles. The shut-in period may vary from a few minutes to several days. The proppant particles of the present invention are particularly suitable for use as propping agents in wells of depths less than about 14,000 feet.

What is claimed is:

1. A low density proppant comprising solid sintered ceramic pellets which prior to sintering consist essentially of a mixture of a kaolin clay and amorphous to microcrystalline silica, said clay being substantially free of quartz and, prior to sintering, having been maintained at a temperature low enough to prevent a phase transformation of said kaolin clay to mullite and crystobalite, said pellets having specific gravity of less than 2.70, such proppant having a conductivity of at least 3,000

md-ft after 50 hours at 8,000 psi and 275° F. in the presence of deoxygenated aqueous 2% solution of KCl as measured by the Stim-Lab Technique using sandstone shims.

2. The proppant of claim 1 wherein said pellets have a specific gravity of 2.6 or less.

3. The proppant of claim 1 wherein said pellets are produced by the method comprising the steps of:

pelletizing an initial amount of material which consists essentially of a mixture of milled, calcined kaolin clay and amorphous to microcrystalline silica by simultaneously mixing and compacting said material while adding water at a controlled rate;

adding additional amounts of said material at a controlled rate while continuing said simultaneous mixing and compacting to form pellets therefrom in a desired size range; and

drying and sintering said pellets.

4. The proppant of claim 3 wherein said step of pelletizing further includes dispersing an organic binder in said material prior to adding water.

5. The proppant of claim 3 wherein said kaolin clay is calcined at a temperature of less than 900° C.

6. The low density proppant of claim 3 wherein said method further includes the steps of:

milling said kaolin clay and said silica to an agglomerated particle size of 7 microns or less.

7. The proppant of claim 6 wherein said calcined kaolin clay and silica are milled together.

8. The low density proppant of claim 6 wherein said calcined kaolin clay and silica are milled to an agglomerated particle size of 3 microns or less.

9. The proppant of claim 5 wherein said kaolin clay is calcined to an LOI of 12 w/o or less when tested at 1400° C.

10. The proppant of claim 9 wherein said kaolin clay is calcined to an LOI of 2 w/o or less when tested at a temperature of 1400° C.

11. The proppant of claim 1 having a conductivity of at least 4,000 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of deoxygenated aqueous 2% solution of KCl as measured by the Stim-Lab Technique using sandstone shims.

12. The proppant of claim 1 wherein said clay contains less than 1% quartz prior to sintering.

13. The proppant of claim 1 consisting essentially of mullite and crystobalite.

14. A low density proppant comprising solid ceramic pellets consisting essentially of mullite and crystobalite and having a dry specific gravity of about 2.6 or less, said proppant having a conductivity of at least 3,000 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of a deoxygenated aqueous 2% solution of KCl as measured by the Stim-Lab Technique using sandstone shims.

15. The low density proppant of claim 14 wherein said proppant has a conductivity of at least 4000 md-ft after 50 hours at 8000 psi and 275° F. in the presence of a deoxygenated aqueous 2% solution of KCl as measured by the Stim-Lab Technique using sandstone shims.

16. The proppant of claim 14 wherein said pellets contain between 35 w/o and 60 w/o mullite, between 35 w/o and 60 w/o crystobalite, and less than 10 w/o of a glassy phase.

17. A low density proppant comprising sintered pellets consisting essentially of mullite and at least 35% crystobalite and which prior to sintering consist essentially of a mixture of between 0 w/o to 90 w/o calcined kaolin clay and 10 w/o to 100 w/o amorphous to microcrystalline silica, said kaolin clay containing less that 2 w/o quartz and less than 1 w/o iron, said mixture being substantially free of mullite and crystobalite prior to sintering, said pellets having a density of less than about 2.6, said calcined kaolin clay and silica having been milled to an average particle size of less than 7 microns.

18. The proppant of claim 17 wherein said calcined kaolin clay and silica were milled to an average particle size of 3 microns or less prior to sintering.

19. The proppant of claim 18 wherein said kaolin clay is calcined to an LOI of less than 12 w/o when tested at 1400° C.

20. The proppant of claim 17 having a conductivity of at least 4,000 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of deoxygenated aqueous 2% solution of KCl as measured by the Stim-Lab Technique using sandstone shims.

21. A low density proppant comprising about from 35 w/o to about 60 w/o mullite and about 35 w/o to about 60 w/o crystobalite, having a specific gravity of less than 2.70, and having a conductivity of at least 3,000 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of deoxygenated aqueous 2% solution of KCl as measured by the Stim-Lab Technique using sandstone shims, with less than 10% of said proppant being a glassy phase.

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EXHIBIT 2

United States Patent [19]

Rumpf et al.

[11] **Patent Number: 4,977,116**

[45] **Date of Patent: Dec. 11, 1990**

[54] **METHOD FOR MAKING LIGHTWEIGHT PROPPANT FOR OIL AND GAS WELLS**

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[21] Appl. No.: **482,632**

[22] Filed: **Feb. 21, 1990**

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[51] **Int. Cl.^{5}** **C04B 35/10**

[52] **U.S. Cl.** **501/128**; 501/127; 501/133; 501/144; 166/280

[58] **Field of Search** 501/127, 128, 133, 144; 166/280

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4,713,203	12/1987	Andrews	264/117
4,921,821	5/1990	Rumpf et al.	501/144 X

FOREIGN PATENT DOCUMENTS

101855	3/1984	European Pat. Off. .
116369	8/1984	European Pat. Off. .
169412	1/1986	European Pat. Off. .
8503327	8/1985	PCT Int'l Appl. .

Primary Examiner—Karl Group

[57] **ABSTRACT**

A lightweight oil and gas well proppant made by simultaneously mixing and compacting a mixture of kaolin clay which has been calcined at a temperature low enough to prevent the formation of mullite and crystobalities to an LOI of 12 or less when tested at 1400° C., and amorphous to microcrystalline silica both of which have been milled to an average agglomerated particle size of 7 microns or less to form green pellets, and then drying, screening and sintering the pellets to form proppant pellets having a specific gravity of 2.7 or less, the proppant having a conductivity of at least 3,000 millidarci-feet as measured by the StimLab Technique after 50 hours at 8,000 psi and 275° F., in the presence of deoxygenated aqueous 2% solution of KCl using sandstone shims.

12 Claims, No Drawings

METHOD FOR MAKING LIGHTWEIGHT PROPPANT FOR OIL AND GAS WELLS

This is a divisional of copending application Ser. No. 07/297,876, filed on Jan. 17, 1989, now U.S. Pat. No. 4,921,820, which is a continuation-in-part of Ser. No. 07/277,258, filed on Aug. 2, 1988, now abandoned.

FIELD OF INVENTION

This invention relates generally to a method of making lightweight proppants for oil and gas wells and more particularly to a method of making lightweight proppants for oil and gas wells which are lighter in weight than existing lightweight proppants but which have strength and conductivity similar to and preferably substantially higher than such existing lightweight proppants.

BACKGROUND

Hydraulic fracturing is a process of injecting fluids into a selected oil or gas bearing subsurface earth formation traversed by a well bore at sufficiently high rates and pressures such that the formation fails in tension and fractures to accept the fluid. In order to hold the fracture open once the fracturing pressure is released a propping agent (proppant) is mixed with the fluid which is injected into the formation.

Hydraulic fracturing increases the flow of fluids from an oil or gas reservoir to a well bore in at least three ways: (1) the overall reservoir area in communication with the well bore is increased, (2) the proppant in the fracture generally has significantly higher permeability than that of the formation, thereby allowing fluids to flow more easily, and (3) the high conductivity channel causes large pressure gradients to be created in the reservoir past the tip of the fracture.

Proppants are generally strong, preferably substantially spherical, particulates that should be able to withstand the high temperatures and pressures and corrosive environments experienced in the subsurface formations surrounding an oil or gas well. Early proppants were formed of material such as glass beads, sand, walnut shells and aluminum pellets. These materials did not have sufficient strength or resistance to corrosion to be successful in many wells, particularly where closure pressures above a few thousand p.s.i. were experienced.

U.S. Pat. No. 4,068,718 to Cooke relates to a proppant which Cooke states is formed of "sintered bauxite" that has a specific gravity greater than 3.4. Cooke states that specific gravities above 3.4 are required in order that the proppant have sufficient compressive strength to resist fragmentation under the high stress levels experienced in use. While the proppant described in Cooke's example proved to have sufficient strength to resist crushing, the high specific gravity was undesirable since it required the use of higher viscosity fracturing fluids and resulted in a lower volumetric proppant concentration for a given weight of proppant loading in a fracturing fluid when compared with that achieved by a proppant of lower specific gravity. In general, the higher the volumetric concentration of the proppant in the fracturing fluid, the wider the propped fracture will be after the fracturing pressure is released.

U.S. Pat. No. 4,427,068 to Fitzgibbon relates to intermediate strength composite proppants made by mixing calcined diaspore clay, burley clay or flint clay with alumina, "bauxite" or mixtures thereof such that the ratio of alumina to silica in the composite mix is between nine to one and one to one. The powdered starting materials are mixed in an Eirich mixer and while the mixing is in progress sufficient water is added to cause formation of composite spherical pellets from the powdered mixture. Fitzgibbon states that the rate of water addition is not critical. The pellets are dried and then furnaced to sinter the pellets. The sintered pellets have a specific gravity of between 2.7 and 3.4.

U.S. Pat. No. 4,522,731 to Lunghofer relates to an intermediate strength proppant having an alumina content between 40% and 60% which is produced using a spray agglomeration process and which has a density of less than 3.0 gr/cc. In a preferred embodiment Lunghofer produces his proppants from "Eufaula bauxite" which it states is bauxitic-kaolin type material deposited in and around Eufaula, Ala. According to Lunghofer, the Eufaula bauxite preferably contains at least some (above 5%) gibbsite.

U.S. Pat. No. 4,668,645 to Khaund relates to an intermediate strength proppant made from a mined "bauxitic clay" having a specified chemical composition.

The proppants described in the Fitzgibbons, Lunghofer and Khaund patents have specific gravities lower than that of the earlier Cooke proppant and proppants having such lower specific gravities have been used with some success in intermediate depth wells where the stress on the proppant is in the 5,000 to 10,000 p.s.i. range. It will be desirable, however, to have still lighter weight proppants which are easier to transport in the fracturing fluid and are therefore carried farther into the fracture before settling out and which will yield a wider propped fracture than the known lower specific gravity proppants. The lighter weight proppant should, however, have a conductivity rating at least as high as and preferably substantially higher than those obtainable with the presently available "lightweight" proppants.

The conductivity of a proppant under specific conditions of stress, temperature, corrosive environment and time is the single most important measure of its quality. The conductivity of a packed proppant such as might be deposited in a fracture is defined as the permeability of the proppant pack multiplied by the width of the propped fracture and is usually stated in units of millidarci-feet ("md-ft").

The conductivity of currently available intermediate strength proppants is frequently measured by the tentative API 8 hour procedure, "Tentative Fifth Draft of Recommended Prac- tices For Evaluating Short Term Proppant Pack Conductivity", (March 1987) (hereinafter the "API 8 hour Procedure"), which procedure is hereby incorporated by reference.

Recently a consortium of some twenty-eight organizations involved in various aspects of the fracturing and stimulation business has sponsored research on ways of evaluating and improving stimulation techniques. Stim-Lab, Inc. of Duncan, Okla. acts as the testing arm of the consortium to develop consistent and repeatable testing procedures for proppants including tests for determining their permeability and conductivity. The long term conductivity testing techniques developed by Stim-Lab have been widely accepted in the industry and are described in a publication of the Society of Petroleum Engineers, No. SPE 16900, entitled "An Evaluation of the Effects of Environmental Conditions and Fracturing Fluids on the Long-Term Conductivity of Proppants" by G.S. Penny of Stim-Lab, Inc., which publication is hereby incorporated by reference. It should be understood that any gap in the description in the SPE publication should be filled in by reference to the API 8 hour Procedure. The testing techniques used by the applicants to determine the conductivity of the proppants of the present invention as they are intended to be supplied to a customer (referred to as the "Stim-Lab Technique") are essentially identical to those described in SPE publication No. 16900 using Monel-K 500 or sandstone shims in the conductivity cells, as noted herein A single cell was used rather than stacking 4 cells in the manner described in the SPE publication. This however should have no effect on the measured results. The Stim-Lab Technique is considered to yield conductivity measurements that are repeatable to within about 5–10%.

SUMMARY OF THE INVENTION

In accordance with the invention there is provided a low density, high strength proppant which is formed of solid ceramic particles having a dry specific gravity less than 2.70 and preferably 2.60 or less and a conductivity of at least about 3,000 md-ft and preferably at least 4000 md-ft after 50 hours at 8,000 p.s.i. and 275° F. in the presence of a deoxygenated 2% aqueous solution of KCl as measured by the Stim-Lab Technique using sandstone shims. Most preferably the conductivity is at least 4400 md-ft as measured under the above conditions.

The method of the present invention involves producing a proppant by milling calcined kaolin clay and an amorphous to microcrystalline silica to an average particle size of less that 7 microns, and preferably about 3.0 microns or less and pelletizing a mixture of the resulting powders in a compacting mixer. Preferably the mixture contains between 55 weight percent ("w/o") and 90 w/o kaolinite and between 45 w/o and 10 w/o silica, although the percentages may fall outside these ranges. Kaolinite is normally the major component of the mixture. However, in the limit the silica content could reach 100% yielding a proppant of essentially all crystobablite having a specific gravity of about 2.33. The kaolinite and silica are preferably milled together

The kaolin clay is calcined at a temperature of less than 900° C. to reduce the loss on ignition ("LOI") to 12 W/o or less when tested at 1400° C., and preferably to about 2 w/o LOI when tested at 1400° C. It is important that the calcining be done at a low enough temperature that the kaolin clay does not undergo a phase transformation to mullite and crystobalite. The silica should not contain any significant amount of crystalline quartz, other than amorphous to microcrystalline quartz as hereinafter defined, and is preferably dried to a LOI of about 1 w/o when tested at 1000° C.

Preferably, an organic binder is first dispersed in the milled material in the mixer and then water is added to the powder at a controlled rate while mixing and compacting the powder to form rough pellets of a desired size. Next, with the mixer still running, additional dry, milled material is slowly added to yield smooth, spherical pellets. The pellets are then dried and fired to convert the material to proppant pellets that preferably comprise between about 35 (w/o) and 60 w/o mullite, between about 35 w/o and 60 w/o crystobalite and a minor amount (less than 10 w/o) of a glassy phase. The proppant has a specific gravity of less than 2.70 and preferably of 2.60 or less. Most preferably the pellets comprise between 35 w/o and 50 w/o mullite and 50 w/o to 60 w/o crystobalite.

The proppant produced in accordance with the method of the present invention is mixed with a fluid and injected into a subterranean formation under high pressure to open a fracture, with the proppant remaining in the fracture to prop it open after the fracturing pressure is removed. The measured conductivity of the proppants of the present invention are equal to and usually substantially better than those of other known lightweight proppants which have higher specific gravities and higher weight per unit of volume.

DETAILED DESCRIPTION

The preferred raw materials for use in making the low specific gravity, high strength proppants of the present invention are kaolin clay and amorphous to microcrystalline silica. Preferably the kaolin clay consists largely of kaolinite ($Al_2Si_{25}(OH)_4$) and is essentially free of sand (i.e., quartz). One source of such material is from C E. Minerals, headquartered in King of Prussia, Pa. The kaolinite deposits owned by C. E. Minerals are mined at C. E. Mineral's Mulcoa operations in Andersonville, Ga. The Andersonville kaolin deposits owned by C. E. Minerals are well described in a report by Alfred D. Zapp entitled "Bauxite Deposits of the Andersonville District, Ga", U.S. Geological Survey Bulletin 1199-G. This report is incorporated herein by reference. The report states that the deposit consists largely of the mineral kaolinite and is essentially sand free. The chief impurities are compounds of iron and titanium and small amounts of gibbsite. The kaolin clay is deposited in tabular lenticular masses. Raw materials containing significant amounts of sand (free silica or quartz) produce a weaker proppant, while raw materials containing gibbsite or other hydrated aluminas yield a product having an undesirably high specific gravity.

By amorphous to microcrystalline silica is meant silica which is truly amorphous or is "amorphous" in the sense that the ultimate submicron particles, as seen with the aid of a scanning electron microscope, do not have the angular shape of crystals. One source of amorphous to microcrystalline silica is from Illinois Minerals Company in Cairo, Ill. This silica, as described by Illinois Minerals, is an extremely fine-grained microcrystalline silica formed by weathering of silica-rich limestone. Materials from other deposits of kaolinite and of amorphous to microcrystalline silica can also be used in making the proppants of the present invention.

In general the kaolin clay most useful as a raw material in making the proppants in accordance with the invention may contain by chemical analysis about 45 w/o alumina and 52 w/o silica, less than 1 w/o iron oxide and less than 2 w/o (preferably less than 1 w/o) free quartz. Preferably the kaoline clay approaches 100% kaolinite. Most preferably the amount of free quartz is non-detectable.

Other naturally occurring minerals which may be present in minor or trace amounts include anatase and rutile. Minerals whose presence in the raw material appear to be somewhat detrimental to the properties of the final product include quartz, pyrite, marcasite, siderite, micas and montmorillonites. The amorphous to microcystalline silica most useful as a raw material in making the proppants in accordance with the invention should contain by chemical analysis at least 94 w/o (preferably 100 w/o) silica.

The kaolin clay is preferably calcined before further processing in order to remove water and organics. In accordance with the invention, applicants have found that the calcining should be performed at a temperature low enough that the kaolin clay does not undergo a phase change to form mullite or crystobalite. Applicants have found that the presence of any significant amount of mullite or crystobalite in the kaolin clay before the final drying and firing steps has a severely detrimental effect on the properties of the proppants produced. Therefore the calcining should be performed at a temperature below 900° C. for a sufficient time that the loss on ignition ("LOI") of the kaolinite is 12 w/o or less and preferably 2 w/o or less when tested at 1400° C. The calcining may be performed relatively quickly at temperatures on the order of 700° to 800° C. or may be performed more slowly at lower temperatures. If the calcining temperature is above about 450° to 500° C., the kaolinite is converted to amorphous alumina and silica (sometimes referred to as "meta kaolinite"). Such a transformation, however, has no adverse effect on the product of the invention. The silica should be dried after mining to an LOI of less than 1 w/o when tested at 1,000° C. This drying is typically done at temperatures of between about 150° and 200° C.

The calcined material and the silica is then reduced in particle size, preferably by dry ball milling them in a closed loop system containing a particle classifier. The average agglomerated particle size in this milled material is less than 7 microns and preferably about 3.0 microns or less as measured by a Sedigraph (Micro Meritics Instrument Corp.) or a Granulometre' (Cilas Compagnie Industrielle des Lasars). The true ultimate particle size, however, of the milled raw material (both the kaolin and silica) is much finer than 3.0 microns and is believed to be made up of submicron flakes or particles. Such submicron flakes or particles tend to agglomerate to form the composite particles which are sensed by the measuring instruments. The calcined kaolin clay and silica are mixed together and preferable are milled together. The mixture preferably contains between 55 w/o and 90 w/o kaolinite and between 45 w/o and 10 w/o silica, although different percentage mixtures may be used. Kaolinite is normally the major component of the mixture. However, in the limit the amorphous to microcrystalline silica content can reach 100%, yielding a proppant that is essentially entirely crystobalite having a specific gravity of about 2.33. Such a super lightweight proppant would be very useful in shallow wells when closure stresses are on the order of 4000 p.s.i. or less.

The milled raw material is pelletized preferably in a compacting mixer. The preferred commercially available machines for this purpose are the Eirich Countercurrent Intensive Mixers which are manufactured in several sizes of different capacities by the Maschinenfabrik Gustav Eirich of Hardheim, West Germany and distributed in the United States by Eirich Machines, Inc., New York, N.Y.

The Eirich mixer has a rotating mixing pan forming the bottom of the mixing chamber which pan can be either horizontal or inclined at an angle and a "mixing star" which rotates in the opposite direction from the pan. The mixing star rotates about an axis parallel to and offset from that of the pan and has a diameter of about 20 to 25 percent of that of the pan. The preferred form of mixing star for the pelletizing operation is referred to by Eirich as a suction type rotor and has a plurality of

vertically extending trapidzoidally shaped mixing elements which extend from the periphery of the rotating element. For the Model R7 machine, the pan has a single rotational speed of about 45 r.p.m., while the mixing star has a low and a high speed. The low speed is about 700 r.p.m. and the high speed is about twice that, about 1400 r.p.m. The rotational speeds of the elements of the larger mixers are adjusted so that rotating elements have similar tip speeds. The mixer may also contain a second mixing star upon which can be mounted plows for cleaning the sides of the rotating pan. This second mixing star is also mounted eccentrically in the mixer and rotates in the opposite direction from the mixing pan. An example of another compacting mixer that is believed suitable for use in the present invention is the Littleford Lodige mixer.

The milled powder charge is preferably first mixed dry in the mixer with up to about 3 w/o (calculated on the basis of the initial milled powder charge) of an organic binder such as gelatinized cornstarch for a period of about 30 seconds with the suction rotor on the low speed setting in order to fully disperse the binder in the raw material powder.

It is preferred that such binders be such that they are pyrolized or driven off during later firing of the proppant pellets. The amount of the binder is normally on the order of 1 w/o to 3 w/o of the initial milled powder charge. It is possible to make pellets with the method of the invention without a binder but it is believed that the use of a binder results in improved properties and yield.

Next water is added at a controlled rate to the mixer with the suction rotor running at the low speed setting to initially pelletize the material. The rate of water addition should be controlled properly to facilitate the formation of the pellets in the mixer and can affect the quality of the final product. Typically the total amount of water for the Model R7 Eirich mixer is from about 35 to 55 w/o of the initial starting material and preferably about 43 to 50 w/o. Preferably between about 40 and 60 w/o of the expected total amount of water is added after the binder is dispersed and mixed for about 2 to 4 minutes. Thereafter additions of about 8 to 10% of the total water are made about every 0.75 to 1.5 minutes until irregularly shaped pellets ranging in size from about 1/16 to ⅛ inch in diameter are formed.

Once pellets have formed in the mixer, which at this point are normally large and irregularly shaped, the suction rotor is switched to the high speed setting and additional milled calcined raw material (referred to as "dust") is slowly added to the mixer over a period of about 5 to 7 minutes in order to cause the pellets to become smaller, well shaped spheres of a narrower size distribution, typically 0.02 inches to 0.047 inches. Typically, the amount of dust required to form the desired size spheres is about 42 to 70 w/o of the starting raw material. Preferably about 46 to 54 w/o dust is added.

In some cases the suction rotor is switched back to the low speed setting for a later portion of the 5 to 7 minute period after a major portion of the dust has been added to the mixer. After adding the dust, the suction rotor is then preferably set back to the low speed setting if it has not already been and the mixer run for a further period of about 30 seconds in order to improve the sphericity of the pellets and to increase yield of the desired size range.

The amount and rate of water and dust additions to the mixer can have a significant impact on the conductivity of the proppant produced by the method of the invention. If too much water is added, the particles are poorly shaped and are too large. If the dust is added too quickly it results in a poor yield of particles in the desired size range. If not enough dust is added the particles are poorly shaped and will stick together in agglomerated masses. If too much dust is added the particles have a rough surface and unconsolidated dust remains in the mixer. When the right amount of dust is added, the process yields smooth, spherical, well compacted pellets. The spherical pellets are next discharged from the mixer and dried to a free moisture content of less than 10% and preferably less than 5%. The drying temperature and time does not appear to be critical and it has been found, for instance, that drying at temperatures of 150° C. overnight, or of 260° C. for 10 to 15 minutes are suitable. Once dried, the desired size spherical pellets are separated by screening for instance to a 18/35 mesh size. The larger than 18 mesh and finer than 35 mesh are recycled to be repelletized. The screened particles in the desired size range are then sintered, for instance in a rotary kiln, at a temperature between 1300° and 1500° C., preferably between 1375° to 1425° C. for about 15 to 30 minutes at temperature. The total time in the kiln is normally from about 1 to 1½ hours. The particles shrink upon firing by about 15% to 20%. The desired finished size is typically between about 0.0167 inches and 0.0331 inches but can be larger or smaller as needed. The particular temperature to which the screened particles are fired is selected in order to maximize their strength. This temperature depends on several variables, some of which are the raw material mineralogy, the milled particle size, the pellet size and the volume of material in the kiln.

After firing, the pellets are again screened to the desired final size. A typical product size is 20/40 mesh which contains 90 w/o of its pellets of between 0.0167 inches and 0.0331 inches in size and preferably 90 w/o of the pellets between about 0.0232 inches and 0.0331 inches in size.

The proppants of the invention have been found to have surprisingly and unexpectedly high conductivities for having such low specific gravities. More particularly, the conductivities of the proppants of the preferred embodiment of the present invention are at least 3000 md-ft and preferably at least 4000 md-ft after 50 hours at 8000 p.s.i. and 275° F. in the presence of a deoxygenated 2% aqueous solution of KCl as measured by the Stim-Lab Technique using sandstone shims. Most preferably the conductivity is at least 4500 md-ft when measured under the above conditions. The proppants of the present invention have specific gravities of less than 2.70, and preferably 2.60 or less, which are lower than those of other commercially available lightweight proppants. In fact, the preferred proppants of the present invention are even lighter than sand (specific gravity 2.64), the lightest proppant which has heretofore been in common commercial use. The conductivity of the proppants of the present invention are between about 3 and 20 times that of sand, however, depending upon operating conditions. Sand is of little use at pressures on the order of 8000 p.s.i. while the preferred proppants of the present invention still have high conductivities, on the order of as much as 4500 md-ft, at such pressures.

Compared to another heavier commercially available proppant which is considered to be in the lightweight range, the preferred proppants of the present invention have substantially higher conductivities. The commercially available "lightweight" proppant has been measured in accordance with the Stim-Lab technique to have a conductivity of 6067 md-ft after 50 hours at 250° F. and 6000 p.s.i. closure stress in the presence of deoxygenated aqueous 2% KCL solution using sandstone shims. A proppant in accordance with the preferred embodiment of the present invention had conductivity values of 7855 md-ft when measured under the same conditions. The same commercially available "lightweight" proppant had conductivities measured by the Stim-Lab technique of 3616 to 3700 md-ft after 50 hours at 275° F. and 8000 p.s.i. while the proppant of the present invention had a conductivity of 4459 md-ft under similar conditions.

The Loose Pack Bulk Density (LPBD) of the proppant of the invention used in the above example is 1.45 gms/cm^3. The LPBD of the commercially available "lightweight" proppant used for comparison in the above example is 1.61 gm/cm^3. Their specific gravities were 2.56 and 2.70 respectively.

From a mineralogical point of view the sintered pellets of the present invention are preferably between about 35 w/o and 60 w/o mullite and between about 38 w/o and 60 w/o crystobalite and a minor amount (less than 10 w/o) of a glassy phase. It is believed that the glassy phase is best minimized for the highest quality product.

EXAMPLES

The invention is further illustrated by reference to the following non-limiting examples wherein all percentages are by weight unless otherwise specified. When applicable calcining conditions and milling techniques for each raw material are given with each example. Unless otherwise indicated, the pellets are screened to an 18/35 mesh size after drying and to a 20/30 mesh size after sintering wherein 90% of the pellets are between about 0.0232 inches and 0.0331 inches in size. The typical yield of properly size pellets in the first screening is about 70%. The chemical compositions of the raw materials used in the following examples are summarized in Table I. The mineralogical composition of the calcined kaolin clays as measured by the X-ray diffraction technique is summarized in Table II. The kaolinite in both the Huber 40-C clay and the Mulcoa clay have been transformed to amorphous alumina and silica by being calcined at 750° C. and thus are no detected by X-ray diffraction. The figures in Tables II for the ACCO clay are for the uncalcined material so that kaolinite is detected. Mineralogically the silicas used in the examples is of such a fine grain size as to be virtually undetectable as measured by X-ray diffraction techniques. The components in Table II are divided into major minerals which comprise about 95 w/o of the detected minerals present and the minor minerals which together make up less then 5 w/o of the detected minerals present. Kaolinite is approximately 45 w/o Al_2O_3. After calcining or drying all the raw materials are milled to an average particle size of about 3 microns as measured by a Granulometre. About 90% of the particles were measured to be less than 10 microns in size.

TABLE I

	1	2	3	4
Example	Huber 40-C Clay	ACCO Clay	Mulcoa Clay	(Silica)
Chemistry				
Al_2O_3	45.0	45.9	43.7	0.7

TABLE I-continued

	1	2	3	4
Example	Huber 40-C Clay	ACCO Clay	Mulcoa Clay	(Silica)
SiO_2	53.0	51.4	51.8	99.0
TiO_2	1.8	1.8	1.7	0.5
Fe_2OO_3	0.2	0.9	0.8	0.5

TABLE II

Example	1	2	3
	Mineralogy		
Major Minerals			
Kaolinite	ND	Major	ND
Minor Minerals			
Anatase	Major	Major	Trace
Rutile	ND	Trace	ND
Quartz	ND	ND	Trace
Mullite	ND	ND	ND
Amorphous	Yes	No	Yes

"ND" means non-detectable

EXAMPLE I

One hundred (100) lbs. of a kaolin clay/silica mixture was produced by combining 86 lbs. of calcined Huber 40-C kaolin clay (manufactured by the J. M. Huber Corporation) and 14 lbs of dried Imsil A-108 microcrystalline silica (manufactured by Illinois Minerals Company) in an Eirich Model R-7 Compacting Mixer and mixing the two ingredients together for 60 seconds. Both the calcined kaokin clay and the silica had been milled separately to an average particle size of 3 microns as measured by a Granulometre. Hereafter in this example this mixture will be referred to as "blended material".

A 50 lbs. charge of blended material was placed in an Eirich Compacting Mixer having an inclined pan and a suction type rotor along with 1½ lbs. of gelatinized cornstarch binder and mixed for 30 seconds with the suction rotor in its low speed setting in order to fully disperse the binder in the blended material. With the suction rotor rotating at its low speed setting, 9 lbs. of water was added to the mixer and mixed for a period of two minutes. As the suction rotor continued to operate in the low speed setting, seven 2 lb. additions, followed by a 1 lb. addition and then a ½ lb. addition of water were added sequentially to the mixer with a 45 second mixing period after each addition. At this point irregularly shaped pellets had formed.

The rotor was then switched to the high speed setting and an additional 17 lbs. of the same blended material was slowly added to the mixer over a three minute period. Then the rotor was reset to its low speed setting and additional 11 lbs. of the blender material was added over a period of two minutes. The mixing was continued with the suction rotor in the low speed setting for an additional period of 30 seconds. At this point the particles had fairly good sphericity but had rather rough surfaces. An additional 7 lbs. of the blended material was slowly added to the mixer over a 1 minute period and the material mixed for an additional 30 seconds with the suction rotor continuing in the low speed setting. The pellets now had a good spherical shape and smooth surfaces. The pellets were discharged from the mixer and dried overnight at 150° C. in a box oven. After drying the pellets were screened to an 18/35 mesh and fired at 1405° C. in a rotary kiln for a period of about 30 minutes at temperature with a total time in the kiln of approximately 1 hour 15 minutes. After cooling the pellets were screened to a 20/30 mesh. The dry specific gravity of the material was 2.56 as measured by a Beckman air comparison pycnometer Model 930.

A conductivity test using the Stim-Lab Technique referred to above was conducted with final closure stress of 6,000 p.s.i. at 250° F. in the presence a deoxygenated aqueous 2% solution of KCl for 50 hours. In accordance with this procedure 63.06 grams of the screened proppant pellets were loaded into a API Hasteloy-C 10 in^2 linear flow cell to give a loading of 2 $lbs./ft^2$ of proppant and leveled loosely with a universal bevel blade device. A 3/8 inch thick sandstone core was placed on top of the test pack followed by an O-ring fitted to a piston which was lightly coated with vacuum grease. The loaded test cell was then placed in a 150 ton Dake press and the closure stress was increased to 500 p.s.i. at a rate of 100 p.s.i./min. The cell was saturated with deoxygenated aqueous 2 w/o KCl solution and then purged of air at the ambient laboratory temperature of 70° F. to 80° F. A Validyne DP15-30 differential pressure transducer connected across the cell was calibrated with water columns to .0001 p.s.i. accuracy. Closure stress was then raised to 1,000 p.s.i. at a rate of 100 p.s.i./min. A Reservoir Accumulator, made up of two 5 gal and two 1 gal nitrogen driven fluid reservoir accumulators which were filled with a 2 w/o KCl aqueous solution that had been deoxygenated with nitrogen to a level of less than 15 ppb and preferably less than 5 ppb of oxygen was connected to the test cell and set at a driving pressure of 400 p.s.i.. The connection of the Reservoir Accumulator to the cell is make through two 150 ml sample cylinders filled with 100 mesh Oklahoma #1 sand with ceramic band heaters in order to saturate the test fluid with silica. It should be noted that the closure stresses on the proppant pack in the cell are stated in terms of the net closure stress on the pack which is equal to the gross pressure applied by the press minus the 400 p.s.i. pressure applied by the reservoir accumulator.

The system was allowed 30 minutes to come to equilibrium and a series of five conductivity measurements were taken and averaged. The conductivity was calculated from the darci relationship:

$$K_{wf}=26.78\mu Q/\delta P \text{ where}$$

k_{wf}=Conductivity (md-ft)

26.78=factor to account for a 1½×5 inch flow area and pressure in p.s.i.

μ=Viscosity of flowing fluid at temperature (cp)

Q=Flow rare (ml/min)

δP=Pressure differential across 5 inch flow path.

After the readings were taken at ambient temperature, the temperature was increased to 250° F. and held for 8 hours for temperature uniformity. Next readings with the system at 250° F. were taken at 1,000 p.s.i., 2,000 p.s.i., 4,000 p.s.i. and 6,000 p.s.i. with the closure stress being raised between levels at a rate of 100 p.s.i./min. After reaching each of the 1,000, 2,000, 4,000 and 6,000 closure stress levels, the system was held at 250° F. for 1.5 hours before the conductivity readings were taken. At the 6,000 p.s.i. level the cell was held at 250° F. for 50 hours during which conductivity measurements were taken at 10 hour intervals. The measured conductivity at the 50 hour time was 7,351 mdft and

7084 md-ft on a second sample of the raw material run at the same time.

EXAMPLE II

In this example a kaolin clay was obtained from the American Cyanamid Co., Andersonville, Ga. The chemical and mineralogical composition of the uncalcined clay as indicated in Table I and II. This kaolin clay was calcined a 480° C. for approximately 24 hours then crushed to less than ⅛". The crushed kaolin clay was combined with 250 grade air-floated microcrystalline silica provided by the Illinois Minerals Company. This mixture contains 75 w/o clay and 25 w/o silica and hereafter will be referred to as "blended material" in this example. The mixture was tumbled in a "V" blender for approximately 2 minutes to insure complete mixing.

The blended material was next reduced in particle size using a jet mill manufactured by the Fluid Energy Processing Equipment Company of Hatfield, Pa. The average particle size of this milled material was 3.68 micons as measured by the Leads and Northrup Microtrac II particle size analyzer.

A 45 lb. charge of this blended material was placed in the Eirich Model R-7 Compacting Mixer described in Example I along with 1½ lbs. of cornstarch binder and mixed dry for 30 seconds at the low speed setting. Water was then added to the mixer with the mixer operating at the low speed setting with 9 lbs. being added and mixed for 2 minutes followed by 4 additions of 2 lbs. each, one addition of 1 lb. and three additions of ½ lb., with a 45 second mixing period after each addition.

The mixer was then set to the high speed mode and 10 lbs. of the blended material was slowly added to the mixer over a minute period. The mixer was then switched back to the low speed setting and an additional 7 lbs. of the blended material was slowly added over a 2 minute period, followed by a 30 second low speed mixing. An additional 3 lbs. of the blended material was added over the following minute followed by an additional 30 second mixing period at the low speed. Then a final 3 lbs. of the blended material was added over the following minute followed by an additional 30 second mixing period at low speed. The particles were thereafter discharged from the mixer and screened, dried and fired in the same manner as described in Example I with the exception that the sintering temperature was 1395° C. After cooling the pellets were screened to a 20-30 mesh size. The dry specific gravity of the material was 2.52. The Stim-Lab conductivity test described in connection with Example I was then performed except that the readings at the elevated temperature where taken at 275° C. and the maximum stress was 8000 p.s.i. The test yielded a measured conductivity after 50 hours at 8,000 p.s.i. and 275° F. of 3,351 md/ft.

EXAMPLE III

In this example a kaolin clay was obtained from C. E. Minerals. This clay was mined at their Mulcoa operation in Andersonville, Ga. The chemical and mineralogical composition of the calcined clay is indicated in Tables I and II. For this example the clay was calcined in a rotary kiln at 750° C. and held at that temperature for 2 hours. This clay was next crushed to minus ⅛ inch then milled in a similar method as the material in Example II. The average particle size of the milled clay in this example was 3.01 microns as measured by the Leads and Northrup Microtrac II. This milled clay was then mixed with Imseil A-108 silica in a similar manner as in Example I, the ratio again being 86% clay and 14% silica. Again as in the previous examples this mixture will be referred to as "blended material" hereafter in this example.

A 45 lbs. charge of this blended material was placed in the Eirich Model R-7 Compacting mixer described in Example I along with 1½ lbs. of cornstarch binder and mixed with water in the same manner as described in Example I with the exception of adding 2 lb. additions to 17 lbs. then 1 lb. additions to 21 lbs. then a ¼ lb. addition.

Next 13 lbs. of blended material was slowly added over a minute period with the mixer in the high speed setting. Next the mixer was switched back to the low speed setting and an additional 8 lbs. of blended material was added over a period of 2 minutes after which the mixer continued to be operated for an additional 30 seconds mixing time. The pellets formed by this procedure were slightly wet but had a good spherical shape. The pellets were then removed from the mixer and dried, screened (both before and after sintering) and sintered in the same sintering temperature used was 1,385° C.

The Stim-Lab conductivity test described in Example II was then performed on the proppant resulting in a conductivity measurement of 4,459 md-ft. after 50 hours at 8,000 p.s.i. at 275° F. The dry specific gravity of the proppant was 2.59.

The low density high strength proppant particles produced in accordance with the method of the present invention may be injected into fractures in subsurface formation as a propping agent. In fracturing treatment a viscous fluid, often referred to as a "pad" is injected into the well at extremely high pressure to cause the formation to fail in tension and fracture to accept the fluid. The fracturing fluid may be an oil base, water base, acid, emulsion, foam or other fluid. Normally the fluid contains several additives such as viscosity builders, drag reducers, fluid loss additives, corrosion inhibitors, cross linkers and the like. The fluid of the pad is injected until a fracture of sufficient geometry is obtained to permit the placement of the proppant pellets. Normally the treatment is designed to provide a fracture at the well bore of at least 2½ times the diameter of the largest proppant pellet. Once a fracture of the desired geommetry is obtained, the proppants are carried suspended in the fluid pad and placed in the fracture. Following placement of the proppant, the well is shut-in for a length of time sufficient to permit the pressure to bleed off into the formation which in turn causes the fracture to close and exert closure stress on the proppant particles. The shutin period may vary from a few minutes to several days. The proppant particles of the present invention are particularly suitable for use as propping agents in wells of depths less than about 14,000 feet.

What is claimed is:

1. A method for making a low density proppant comprising the steps of:

calcining kaolin clay at a temperature below that which would cause the transformation of any significant portion of said kaolin clay to mullite or crystobalite for a time sufficient to reduce the LOI thereof to 12% or less, when tested at 1400° C.;

mixing said calcined kaolin clay with amorphous to microcrystalline silica;

pelletizing said mixture to form pellets in a selected size range; and

sintering said pellets to form proppant particles having a dry specific gravity of less than 2.70.

2. The method of claim 1 further including the step of milling said calcined kaolin clay and said silica to an agglomerated particle size of 7 microns or less prior to the pelletizing step.

3. The method of claim 2 wherein said calcined kaolin clay and silica are milled to an agglomerated particle size of 3 microns or less.

4. The method of claims 1 wherein said calcining is performed at a temperature of less than 900° C. for a time sufficient to reduce the LOI of the kaolin clay to 2 w/o or less at 1400° C.

5. The method of claim 1 wherein said step of pelletizing includes the steps of:

pelletizing an initial amount of material which consists essentially of a mixture of milled, calcined kaolin clay and amorphous to microcrystalline silica by simultaneously mixing and compacting said material while adding water at a controlled rate; and

adding additional amounts of said material at a controlled rate while continuing said simultaneous mixing and compacting to form pellets therefrom in a desired size range.

6. The method of claim 5 wherein said step of pelletizing further includes dispersing an organic binder in said material prior to adding water.

7. The method of claim 5 wherein the amount of water added is between 35 w/o and 50 w/o of said initial amount of material.

8. The method of claim 7 wherein the said additional amounts of said material is between 42 w/o and 70 w/o of the initial amount of said material.

9. The method of claim 1 wherein said proppant has a conductivity at least 3000 md-ft after 50 hours at 8000 p.s.i. and 275° F. in the presence of deoxygenated aqueous 2% solution of KCl as measured by the Stim-Lab Technique using sandstone shims.

10. The method of claim 9 wherein said conductivity is at least 4000 md-ft.

11. A method for making a low density proppant comprising the steps of:

providing a powder mixture of between 0 and 90 w/o calcined kaolin clay and between 10 and 100 w/o of amorphous to microcrystalline silica, said calcined kaolin clay containing less than 2 w/o quartz, said calcined kaolin clay and silica having been milled to an average agglomerated particle size of less than 7 microns;

pelletizing said powder mixture by simultaneously mixing and compacting said mixture while adding water at a controlled rate and adding additional amounts of said mixture while continuing said simultaneous mixing and compacting, to form pellets in a selected size range; and

drying and sintering said pellets to form proppant particles having a specific gravity of 2.60 and of less.

12. The method of claim 11 wherein said calcined kaolin clay is calcined at a temperature low enough such that substantially none of said kaolin clay is transformed to mullite or crystobalite during calcining.

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EXHIBIT 3

United States Patent [19]

Rumpf et al.

[11] **Patent Number: 5,030,603**

[45] **Date of Patent: Jul. 9, 1991**

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[54] **LIGHTWEIGHT OIL AND GAS WELL PROPPANTS**

[75] Inventors: **David S. Rumpf**, North Tonawanda, N.Y.; **Paul R. Lemieux**, Forth Smith, Ark.

[73] Assignee: **Norton-Alcoa**, Ft. Smith, Ark.

[21] Appl. No.: **483,256**

[22] Filed: **Feb. 21, 1990**

Related U.S. Application Data

[60] Division of Ser. No. 297,877, Jan. 17, 1989, Pat. No. 4,921,821, which is a continuation-in-part of Ser. No. 277,258, Aug. 2, 1988, abandoned.

[51] **Int. Cl.**^{5} **C04B 35/10**

[52] **U.S. Cl.** **501/127**; 501/128; 501/133; 501/144; 166/280

[58] **Field of Search** 501/127, 128, 133, 144; 166/280

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[57] **ABSTRACT**

A lightweight oil and gas well proppant made by simultaneously mixing and compacting a milled calcined kaolin clay powder to form green pellets and then drying, screening and sintering the pellets to form proppant pellets having a specific gravity of 3.0 or less and a conductivity of at least 4,200 millidarci-feet and preferably at least 5,100 md-ft as measured by the Stim-Lab method after 50 hours at 8,000 psi and 275° F. in the presence of deoxygenated aqueous 2% solution of KCl.

20 Claims, No Drawings

LIGHTWEIGHT OIL AND GAS WELL PROPPANTS

This application is a division of application Ser. No. 07/297,877, filed Jan. 17, 1989, now U.S. Pat. No. 4,921,821 which, in turn, is a continuation-in-part of application Ser. No. 07/277,258, filed Aug. 2, 1988, now abandoned.

FIELD OF INVENTION

This invention relates generally to lightweight proppants for oil and gas wells and more particularly to lightweight proppants for oil and gas wells having increased strength and conductivity.

BACKGROUND

Hydraulic fracturing is a process of injecting fluids into a selected oil or gas bearing subsurface earth formation traversed by a well bore at sufficiently high rates and pressures such that the formation fails in tension and fractures to accept the fluid. In order to hold the fracture open once the fracturing pressure is released a propping agent (proppant) is mixed with the fluid which is injected into the formation.

Hydraulic fracturing increases the flow of fluids from an oil or gas reservoir to a well bore in at least three ways: (1) the overall reservoir area in communication with the well bore is increased, (2) the proppant in the fracture generally has significantly higher permeability than that of the formation, thereby allowing fluids to flow more easily, and (3) the high conductivity channel causes large pressure gradients to be created in the reservoir past the tip of the fracture.

Proppants are generally strong, preferably substantially spherical, particulates that should be able to withstand the high temperatures and pressures and corrosive environments experienced in the subsurface formations surrounding an oil or gas well. Early proppants were formed of material such as glass beads, sand, walnut shells and aluminum pellets. These materials did not have sufficient strength or resistance to corrosion to be successful in many wells, particularly where closure pressures above a few thousand psi were experienced.

U.S. Pat. No. 4,068,718 to Cooke relates to a proppant which Cooke states is formed of "sintered bauxite" that has a specific gravity greater than 3.4. Cooke states that specific gravities above 3.4 are required in order that the proppant have sufficient compressive strength to resist fragmentation under the high stress levels experienced in use. While the proppant described in Cooke's example proved to have sufficient strength to resist crushing, the high specific gravity was undesirable since it required the use of higher viscosity fracturing fluids and resulted in a lower volumetric proppant concentration for a given weight of proppant loading in a fracturing fluid when compared with that achieved by a proppant of lower specific gravity In general, the higher the volumetric concentration of the proppant in the fracturing fluid the wider the propped fracture will be after the fracturing pressure is released.

U.S. Pat. No. 4,427,068 to Fitzgibbon relates to intermediate strength composite proppants made by mixing calcined diaspore clay, burley clay or flint clay with alumina, "bauxite" or mixtures thereof such that the ratio of alumina to silica in the composite mix is between nine to one and one to one. The powdered starting materials are mixed in an Eirich mixer and while the mixing is in progress sufficient water is added to cause formation of composite spherical pellets from the powdered mixture. Fitzgibbon states that the rate of water addition is not critical. The pellets are dried and then furnaced to sinter the pellets The sintered pellets have a specific gravity of between 2.7 and 3.4.

U.S. Pat. No. 4,522,731 to Lunghofer relates to an intermediate strength proppant having an alumina content between 40% and 60% which is produced using a spray agglomeration process and which has a density of less than 3.0 gr/cc. In a preferred embodiment Lunghofer produces his proppants from "Eufaula bauxite" which it states is bauxitic-kaolin type material deposited in and around Eufaula, Alabama. According to Lunghofer, the Eufaula bauxite preferably contains at least some (above 5%) gibbsite.

U.S. Pat. No. 4,668,645 to Khaund relates to an intermediate strength proppant made from a mined "bauxitic clay" having a specified chemical composition.

The proppants described in the Fitzgibbons, Lunghofer and Khaund patents have specific gravities lower than that of the earlier Cooke proppant and proppants having such lower specific gravities have been used with some success in intermediate depth wells where the stress on the proppant is in the 5,000 to 10,000 psi range. These lower specific gravity proppants, however, all have compressive strengths which are substantially lower than that of high specific gravity materials such as that referred to in the Cooke, et al. patent, which limits the conductivities and permeabilities that are obtained with such proppants, particularly at closure pressures over about 10,000 psi.

The conductivity of a proppant under specific conditions of stress, temperature, corrosive environment and time is the single most important measure of its quality. The conductivity of a packed proppant such as might be deposited in a fracture is defined as the permeability of the proppant pack multiplied by the width of the propped fracture and is usually stated in units of millidarci-feet ("md-ft").

The conductivity of currently available intermediate strength proppants is frequently measured by the tentative API 8 hour procedure, "Tentative Fifth Draft of Recommended Practices For Evaluating Short Term Proppant Pack Conductivity", (March 1987) (hereinafter the "API 8 hour Procedure"), which procedure is hereby incorporated by reference.

Recently a consortium of some twenty-eight organizations involved in various aspects of the fracturing and stimulation business has sponsored research on ways of evaluating and improving stimulation techniques. Stim-Lab, Inc. of Duncan, OK acts as the testing arm of the consortium to develop consistent and repeatable testing procedures for proppants including tests for determining their permeability and conductivity. The long term conductivity testing techniques developed by Stim-Lab have been widely accepted in the industry and are described in a publication of the Society of Petroleum Engineers, No. SPE 6900, entitled "An Evaluation of the Effects of Environmental Conditions and Fracturing Fluids on the Long-Term Conductivity of Proppants" by G. S. Penny of Stim-Lab, Inc., which publication is hereby incorporated by reference. It should be understood that any gap in the description in the SPE publication should be filled in by reference to the API 8 hour Procedure. The testing techniques used by the applicants to determine the conductivity of the proppants of the present invention as they are intended to be supplied to a customer (referred to as the "Stim-Lab Technique") are essentially identical to those described in SPE publication No. 16900 using Monel-K 500 shims in the conductivity cells. A single cell was used rather than stacking 4 cells in the manner described in the SPE publication. This however should have no effect on the measured results. The Stim-Lab Technique is considered to yield conductivity measurements that are repeatable to within about 5-10%.

SUMMARY OF THE INVENTION

In accordance with the invention there is provided a low density, high strength proppant which is formed of solid ceramic particles having a dry specific gravity between 2.65 and 3.0 and preferably between 2.65 and 2.85 and a conductivity of at least about 4000 md-ft and preferably at least 4400 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of a deoxygenated 2% aqueous solution of KCl as measured by the Stim-Lab Technique. Most preferably the conductivity is at least 5500 md-ft as measured under the above conditions.

The proppant of the invention may be produced by milling or other comminuting calcined kaolin clay to an average agglomerated particle size of about 8 microns or less, and preferably of 5 microns or less, and pelletizing said powder in a compacting mixer. The kaolin clay is calcined at a temperature of less than 900° C. to reduce the loss on ignition ("LOI") to 12 w/o or less when tested at 1400° C. Applicants have found in accordance with the invention that it is important that the calcining be done at a low enough temperature that the kaolin clay does not undergo a phase transformation to mullite and crystobalite during such calcining.

Preferably, an organic binder is first dispersed in the milled kaolin clay in the mixer and then water is added to the powder at a controlled rate while mixing and compacting the powder to form rough pellets of a desired size. Next, with the mixer still running, additional dry, milled kaolin clay powder is slowly added to yield smooth, spherical pellets. The pellets are then dried and fired to convert the material to proppant pellets that preferably comprise between about 60 weight percent (hereinafter "w/o") and 85 w/o mullite, between about 15 w/o and 35 w/o crystobalite and a minor amount (less than 10 w/o) of a glassy phase and having a specific gravity of between 2.65 and 3.0.

The proppant of the present invention is mixed with a fluid and injected into a subterranean formation under high pressure to open a fracture, with the proppant remaining in the fracture to prop it open after the fracturing pressure is removed. Surprisingly and unpredictably, the measured conductivities of the proppants of the present invention are up to 100% higher than those of other known intermediate strength proppants, even ones which have higher specific gravities.

DETAILED DESCRIPTION

The preferred raw material for use in making the low specific gravity, high strength proppants of the present invention is kaolin clay. Preferably the kaolin clay consists largely of kaolinite ($Al_2Si_2O_5(OH)_4$) and is essentially free of sand (i.e., quartz). One source of such material is from the American Cyanamid Company in Andersonville, Ga. The Andersonville kaolin deposits owned by American Cyanamid are well described in a report by Alfred D. Zapp entitled "Bauxite Deposits of the Andersonville District, Ga.", U.S. Geological Survey Bulletin 1199-G. This report is incorporated herein by reference. The report states that the deposit consists largely of the mineral kaolinite and is essentially sand free. The chief impurities are compounds of iron and titanium and small amounts of gibbsite. The kaolin clay is deposited in tabular lenticular masses, the thicker of which may have cores of bauxite or bauxitic clay. Raw materials containing significant amounts of sand (free silica or quartz) produce a weaker proppant, while raw materials containing too much gibbsite or other hydrated aluminas yield a product having an undesirably high specific gravity. Another source of material believed to be suitable is the kaolin clay mined at the Mulcoa operations in Andersonville, Ga. of C. E. Minerals, headquartered in King of Prussia, Pa.

In general the kaolin clay most useful as a raw material in making the proppants in accordance with the invention may contain by chemical analysis between about 43 w/o to 58 w/o alumina, about 37 w/o to 52 w/o silica, less than 2 w/o (preferably less than 1 w/o) iron oxide and less than 5 w/o free quartz. Preferably, the kaolin clay comprises between 70 w/o and 90 w/o kaolinite, between 5 w/o and 25 w/o cryptocrystalline to amorphous gibbsite and less than 5 w/o other crystalline materials.

Preferably the amount of free quartz is less than 2 w/o and most preferably is non-detectable. Other naturally occurring minerals which may be present in minor or trace amounts include anatase and rutile. Minerals whose presence in the raw material appear to be somewhat detrimental to the properties of the final product include quartz, pyrite, marcasite, siderite, micas and montmorillonites.

The raw material is preferably calcined before further processing in order to remove water and organics. In accordance with the invention, applicants have found that the calcining should be performed at a temperature low enough that the kaolin clay does not undergo a phase change to form mullite or crystobalite. Applicants have found that the presence of any significant amount of mullite or crystobalite in the kaolin clay before the final drying and firing steps has a severely detrimental effect on the properties of the proppants produced. Therefore the calcining should be performed at a temperature below 900° C. for a sufficient time that the loss on ignition ("LOI") of the kaolinite is 12 w/o or less when tested at 1400° C. The calcining may be performed relatively quickly at temperatures on the order of 700° to 800° C. or may be performed more slowly at lower temperatures. If the calcining temperature is above about 450° to 500° C., the kaolinite is converted to amorphous alumina and silica (sometimes referred to as "meta kaolinite"). Such a transformation, however, has no adverse effect on the product of the invention.

The calcined material is then reduced in particle size, preferably by dry ball milling in a closed loop system containing a particle classifier. The average agglomerated particle size in this milled material should be about 8 microns or less, and preferably 5 microns or less, as measured by a Sedigraph (Micro Meritics Instrument Corp.) or a Granulometer' (Cilas Compagnie Industrielle des Lasars). The true ultimate particle size, however, of the milled raw material is much finer than 8 or 5 microns and is believed to be made up of submicron flakes. Such submicron flakes tend to agglomerate to form composite particles on the order of 8 microns or less which are sensed by the measuring instruments.

The milled raw material is pelletized in a compacting mixer. The preferred commercially available machines for this purpose are the Eirich Countercurrent Intensive Mixers which are manufactured in several sizes of different capacities by the Maschinenfabrik Gustav Eirich of Hardheim, West Germany and distributed in the United States by Eirich Machines, Inc., New York, N.Y.

The Eirich mixer has a rotating mixing pan forming the bottom of the mixing chamber which pan can be either horizontal or inclined at an angle and a "mixing star" which rotates in the opposite direction from the pan. The mixing star rotates about an axis parallel to and offset from that of the pan and has a diameter of about 20 to 25 percent of that of the pan. The preferred form of mixing star for the pelletizing operation is referred to by Eirich as a suction type rotor and has a plurality of vertically extending trapidzoidally shaped mixing elements which extend from the periphery of the rotating element. For the Model R7 machine, the pan has a single rotational speed of about 45 rpm, while the mixing star has a low and a high speed. The low speed is about 700 rpm and the high speed is about twice that, about 1400 rpm. The rotational speeds of the elements of the larger mixers are adjusted so that rotating elements have similar tip speeds. The mixer may also contain a second mixing star upon which can be mounted plows for cleaning the sides of the rotating pan. This second mixing star is also mounted eccentrically in the mixer and rotates in the opposite direction from the mixing pan. An example of another compacting mixer that is believed suitable for use in the present invention is the Littleford Lodige mixer.

The milled, calcined kaolin clay powder charge is preferably first mixed dry in the mixer with about to 2 w/o (calculated on the basis of the initial kaolin clay powder charge) of an organic binder such as a gelatinized cornstarch for a period of about 30 seconds with the suction rotor on the low speed setting in order to fully disperse the binder in the raw material powder.

It is preferred that such binders be such that they are pyrolized or driven off during later firing of the proppant pellets. The amount of the binder is normally on the order of 1 w/o to 2 w/o of the initial kaolin clay powder charge. It is possible to make pellets with the method of the invention without a binder but it is believed that the use of a binder results in improved properties and yield.

Next water is added at a controlled rate to the mixer with the suction rotor running at the low speed setting to initially pelletize the material. The rate of water addition should be controlled properly to facilitate the formation of the pellets in the mixer and can affect the quality of the final product. Typically the total amount of water for the Model R7 Eirich mixer is from about 32 to 40 w/o of the initial starting material and preferably about 35 to 40 w/o. Preferably between about 40 and 60 w/o of the expected total amount of water is added after the binder is dispersed and mixed for about 2 to 4 minutes. Thereafter additions of about 8 to 10% of the total water are made about every 0.75 to 1.5 minutes until irregularly shaped pellets ranging in size from about ⅛ to ¼ inch in diameter are formed.

Once pellets have formed in the mixer, which at this point are normally large and irregularly shaped, the suction rotor is switched to the high speed setting and additional milled calcined raw material (referred to as "dust") is slowly added to the mixer over a period of about 5 minutes in order to cause the pellets to become smaller, well shaped spheres of a narrower size distribution, typically 0.02 inches to 0.047 inches. Typically, the amount of dust required to form the desired size spheres is about 32 to 50 w/o of the starting raw material. Preferably about 40 to 45 w/o dust is added.

In some cases the suction rotor is switched back to the low speed setting for a later portion of the 5 minute period after a major portion of the dust has been added to the mixer. After adding the dust, the suction rotor is then preferably set back to the low speed setting if it has not already been and the mixer run for a further period of about 30 seconds in order to improve the sphericity of the pellets and to increase yield of the desired size range.

The amount and rate of water and dust additions to the mixer can have a significant impact on the conductivity of the proppant produced by the method of the invention. If too much water is added, the particles are poorly shaped and are too large. If the dust is added too quickly it results in a poor yield of particles in the desired size range. If not enough dust is added the particles are poorly shaped and will stick together in agglomerated masses. If too much dust is added the particles have a rough surface and unconsolidated dust remains in the mixer. When the right amount of dust is added, the process yields smooth, spherical, well compacted pellets. It has been found that mixing times towards the lower end of the above stated time ranges during the addition of water in the mixer tend to yield proppants having conductivities of about up to 30 percent higher than if the mixing times are towards the high end of those ranges.

The spherical pellets are next discharged from the mixer and dried to a free moisture content of less than 10% and preferably less than 5%. The drying temperature and time does not appear to be critical and it has been found, for instance, that drying at temperatures of 150° C. overnight, or of 260° C. for 10 to 15 minutes are suitable. Once dried, the desired size spherical pellets are separated by screening for instance to a 18/35 mesh size. The larger than 18 mesh and finer than 35 mesh are recycled to be repelletized. The screened particles in the desired size range are then sintered, for instance in a rotary kiln, at a temperature between 1300° and 1500° C., preferably between 1400° to 1470° C. for about 15 to 30 minutes at temperature. The total time in the kiln is normally from about 1 to ½ hours. The particles shrink upon firing by about 15% to 20%. The desired finished size is between 0.0167 inches and 0.0331 inches but can be larger or smaller as needed. The particular temperature to which the screened particles are fired is selected in order to maximize their strength. This temperature depends on several variables, some of which are the raw material mineralogy, the milled particle size, the pellet size and the volume of material in the kiln.

After firing, the pellets are again screened to the desired final size. A typical product size is 20/40 mesh which contains 90 w/o of its pellets of between 0.0167 inches and 0.0331 inches in size and preferably 90 w/o of the pellets between 0.0232 inches and 0.0331 inches in size.

Surprisingly and unexpectedly, it has been found that the proppants of the present invention have conductivities that are up to 100% higher than previously known intermediate strength proppants, even ones of higher specific gravities. The conductivities of the proppants of the preferred embodiment of the present invention are at least 4000 md-ft, and preferably at least 4400 md-ft, after 50 hours at 8000 psi and 275° F. in the presence of a deoxygenated 2% aqueous solution of KCl as measured by the Stim-Lab Technique. Most preferably the conductivity is at least 5500 md-ft when measured under the above conditions. The proppants of the preferred embodiment of the present invention have dry specific gravities of between 2.65 and 3.0 and preferably between 2.65 and 2.85.

For example, one proppant in wide commercial use which is believed to have been made by the method described in the above referred to Lunghofer patent from starting materials which are very similar to those referred to in that patent have been measured in accordance with the Stim-Lab Technique to have conductivities between 3,057 md-ft and 3700 md-ft after 50 hours at 275° F. and 8,000 psi in the presence of a deoxygenated aqueous 2% KCl solution. The proppants of the following Examples of the present invention, on the other hand, have conductivities between about 4080 md-ft and 6,878 md-ft depending on starting materials and processing conditions when measured under the same conditions.

While the reasons for the dramatically higher conductivities of the proppants of the present invention over those of the prior art are not fully understood, it is believed that they may relate in substantial part to a combination of factors such as the mineralogy and microstructure of the proppant pellets and to the fact that the proppant of the present invention is made from a nearly pure kaolinite raw material which has been calcined at low enough temperatures that it is not then converted to mullite and crystobalite and which has been milled to a fine particle size and then formed into pellets with compaction. In contrast, in the technique of the Lunghofer patent, the raw material is not calcined or milled prior to forming the pellets and the fluidized bed technique used to form the pellets does not provide any compaction during formation.

From a mineralogical point of view the sintered pellets of the preferred embodiment of the present invention are between about 60 w/o and 85 w/o mullite and between about 15 w/o and 35 w/o crystobalite and between about 0 w/o and 10 w/o of a glassy phase. It is believed that the glassy phase is best minimized for the highest quality product.

While the measured specific gravity of the above referred to commercially available proppant is slightly lower than the proppants of the present invention to which it was compared (2.70 vs. 2.80 to 2.90, respectively), this slight difference in density does not explain increases in conductivity of up to 100% and more. This is especially so in light of the fact that intermediate strength proppants such as Interprop Plus and Interprop 1 manufactured by the assignee of the present invention which have specific gravities of about 3.17, have been measured by the same technique to have conductivities of 3808 md-ft and 3269 md-ft, respectively. Thus, even though the proppant of the present invention has a specific gravity lower than that of the Interprop Plus and Interprop 1 proppants, its conductivity is up to more than 80% higher than Interprop Plus and 110% higher than Interprop 1. The Interprop Plus and Interprop 1 proppants are made with different raw materials but with a compacting mixer technique.

EXAMPLES

The invention is further illustrated by reference to the following non-limiting examples wherein all percentages are by weight unless otherwise specified. All of the

raw materials have been calcined at a temperature of 480° C. for a period of approximately 24 hours to an LOI of between 11.0 and 12.1 when tested at 1400° C., and have been ball milled in a Conical closed circuit ball mill with a gyrotor air classifier manufactured by Mineral Processing Systems, Inc. in York, Pa. Unless otherwise indicated, the pellets are screened to an 18/35 mesh size after drying and to a 20/30 mesh size after sintering wherein 90% of the pellets are between 0.0232 inches and 0.0331 inches in size. The typical yield of properly sized pellets in the first screening is about 70%. The chemical compositions of the calcined kaolin clay powders used as raw materials in Examples 1–4 are summarized in Table I. The mineralogical composition of such raw materials as measured by the X-ray diffraction tecnhique is summarized in Table II. It should be noted that in addition to the components listed in Table II, the raw material powders also contain cryptocrystalline to amorphous gibbsite and perhaps other non-crystalline materials which are not detected by the X-ray diffraction technique. In the components in Table II which divide into major minerals which comprise about 95 w/o of the detected minerals present and the minor minerals which together make up less then 5 w/o of the detected minerals present. The amount of gibbsite present can be determined from Table II since in all but Example 3 the amount of SiO_2 present as free quartz is non-detectable so that any Al_2O_3 present which is not part of the kaolinite is believed to be in the form of cryptocrystalline to amorphous gibbsite. Kaolinite is approximately 45 w/o Al_2O_3.

TABLE I

	Example			
Chemistry	1	2	3	4
Al_2O_3	57.14	57.14	48.76	49.29
SiO_2	38.66	38.66	47.76	48.70
Fe_2O_3	1.19	1.19	.94	.90
TiO_2	2.82	2.82	2.18	1.95
CaO	.08	.08	.07	.03
MgO	.03	.03	.03	.03
Na_2O	.04	.04	.12	.04
K_2O	.04	.04	.14	.06

TABLE II

	Example			
Mineralogy	1	2	3	4
Major Minerals				
Kaolinite	Major	Major	Major	Major
Quartz	ND	ND	Minor	ND
Gamma Fe_2O_3	ND	ND	ND	Trace
Minor Minerals				
Anatase	Major	Major	Trace	Minor
Rutile	Trace	Trace	Trace	0

Where 'ND' means non-detectable

EXAMPLE I

A 50 lb. charge of milled, calcined kaolin clay obtained from the American Cyanamid, Andersonville, Ga. deposits and having the chemical and mineralogical composition indicated in Tables I and II was placed in an Eirich Model R7 Compacting Mixer having an inclined pan and a suction type rotor along with 1 lb. of gelatinized cornstarch binder and mixed for 30 seconds with the suction rotor in its low speed setting in order to fully disperse the binder in the kaolin clay powder. With the suction rotor rotating at its low speed setting, 9 lbs. of water was added to the mixer and mixed for a period of two minutes. As the suction rotor continued to operate in the low speed setting, four 2 lb. additions, followed by two 1 lb. additions and a ½ lb. addition of water were added sequentially to the mixer with a 45 second mixing period after each addition. At this point irregularly shaped pellets had formed.

The rotor was then switched to the high speed setting and an additional 12 lbs. of the same milled, calcined kaolin clay powder was slowly added to the mixer over a three minute period. Then the rotor was reset to its low speed setting and additional 6 lbs. of the kaolin clay powder was added over a period of two minutes. The mixing was continued with the suction rotor in the low speed setting for an additional period of 30 seconds. At this point the particles had fairly good sphericity but had rather rough surfaces. An additional 2 ½ lbs. of the kaolin clay powder were slowly added to the mixer over a 1 minute period and the material mixed for an additional 30 seconds with the suction rotor continuing in the low speed setting. The pellets now had a good spherical shape and smooth surfaces. The pellets were discharged from the mixer and dried overnight at 150° C. in a box oven. After drying the pellets were screened to an 18/35 mesh and fired at 1470° C. in a rotary kiln for a period of about 30 minutes at temperature with a total time in the kiln of approximately 1 hour 15 minutes. After cooling the pellets were screened to a 20/30 mesh. The dry specific gravity of the material was 2.90 as measured by a Beckman air comparison pycnometer Model 930.

A conductivity test using the Stim-Lab Technique referred to above was conducted with final closure stress of 8,000 psi at 275° F. in the presence a deoxygenated aqueous 2% solution of KCl for 50 hours. In accordance with this procedure 63.06 grams of the screened proppant pellets were loaded into a API Hasteloy-C 10 in^2 linear flow cell to give a loading of 2 lbs./ft^2 of proppant and leveled loosely with a universal bevel blade device. A 0.030" thick Monel shim was placed on top of the test pack followed by an O ring fitted to a piston which was lightly coated with vacuum grease. The loaded test cell was then placed in a 150 ton Dake press and the closure stress was increased to 500 psi at a rate of 100 psi/min. The cell was saturated with deoxygenated aqueous 2 w/o KCl solution and then purged of air at the ambient laboratory temperature of 70° F. to 80° F. A Validyne DP15-30 differential pressure transducer connected across the cell was calibrated with water columns to 0.0001 psi accuracy. Closure stress was then raised to 1,000 psi at a rate of 100 psi/min. A Reservoir Accumulator, made up of two 5 gal and two 1 gal nitrogen driven fluid reservoir accumulators which were filled with a 2 w/o KCl aqueous solution that had been deoxygenated with nitrogen to a level of less than 15 ppb and preferably less than 5 ppb of oxygen was connected to the test cell and set at a driving pressure of 400 psi. The connection of the Reservoir Accumulator to the cell is make through two 150ml sample cylinders filled with 100 mesh Oklahoma #1 sand with ceramic band heaters in order to saturate the test fluid with silica. It should be noted that the closure stresses on the proppant pack in the cell are stated in terms of the net closure stress on the pack which is equal to the gross pressure applied by the press minus the 400 psi pressure applied by the reservoir accumulator.

The system was allowed 30 minutes to come to equilibrium and a series of five conductivity measurements were taken and averaged. The conductivity was calculated from the darci relationship:

$$k_{wf}=26.78\ \mu Q/\delta P \text{ where}$$

k_{wf}=Conductivity (md-ft)

26.78=factor to account for a 1 ½×5 inch flow area and pressure in psi

μ=Viscosity of flowing fluid at temperature (cp)

Q=Flow rate (ml/min)

δP=Pressure differential across 5 inch flow path.

After the readings were taken at ambient temperature, the temperature was increased to 275° F. and held for 8 hours for temperature uniformity. Next readings with the system at 275° F. were taken at 1,000 psi, 2,000 psi, 4,000 psi, 6,000 psi and 8,000 psi with the closure stress being raised between levels at a rate of 100 psi/min. After reaching each of tbe 1,000, 2,000, 4,000 and 6,000 closure stress levels, the system was held at 275° F. for 1.5 hours before the conductivity readings were taken. At the 8,000 psi level the cell was held at 275° F. for 50 hours during which conductivity measurements were taken at 10 hour intervals. The measured conductivity at the 50 hour time was 6,247 md-ft.

EXAMPLE II

The same Stim-Lab conductivity test procedure described in Example I was repeated on proppant particles made in Example I. This time the measured conductivity at the 50 hour time was 6,878 md-ft.

EXAMPLE III

In this example kaolin clay, designated as SR105 Stardis, obtained from Alcoa Corporation and having the chemical and mineralogical composition indicated in Tables I and II was utilized. A 50 lb. charge of milled, calcined kaolin clay was placed in the Eirich Model R7 Compacting Mixer described in Example I along with 1 lb. of cornstarch binder and mixed dry for 30 seconds at the low speed setting. Water was then added to the mixer with the mixer operating at the low speed setting with 9 lbs. being added and mixed for 4 minutes followed by 4 additions of 2 lbs. each and a final addition of ½ lb., with 1.5 minute mixing period after each addition.

The mixer was then set to the high speed mode and 1 lbs. of the same milled, calcined kaolin clay powder was slowly added to the mixer over a 3 minute period. The mixer was then switched back to the low speed setting and an additional 7 lbs. of the same kaolin clay powder was slowly added over a 2 minute period, followed by a 30 second low speed mixing. An additional 3 ½ lbs. of the same kaolin clay powder was added over the following minute followed by an additional 30 second mixing period at the low speed. Then a final 3 lbs. of the kaolin clay powder was added over the following minute. The particles were thereafter discharged from the mixer and screened, dried and fired in the same manner as described in Example I with the exception that the sintering temperature was 1420° C. After cooling the pellets were screened to a 20–30 mesh size. The dry specific gravity of the material ws 2.80. The Stim-Lab conductivity test described in connection with Example I was then performed yielding a measured conductivity after 50 hours at 8,000 psi and 275° F. of 4,080 md/ft.

EXAMPLE IV

A 50 lb. charge of milled, calcined kaolin clay obtained from the American Cyanamid Andersonville, Ga. deposits having the chemical and mineralogical composition indicated in Tables I and II was placed in the Eirich Model R7 Compacting Mixer described in Example I along with 1 lb. of the cornstarch binder and mixed with water in the same manner as described in Example I with the exception that the final ½ lb. addition of water was eliminated so that only 19 lbs. of water was added to the mixer. At that point the powder had formed into slightly wet looking somewhat irregularly shaped pellets.

Next the mixer was switched to the high speed setting and 15 lbs. of the same milled, calcined kaolin clay powder was slowly added over a 3 minute period. Next the mixer was switched back to the low speed setting and an additional 7 ½ lbs. of the kaolin clay powder was added over the following 2 minutes after which the mixer continued to be operated for an additional 30 second period. The pellets formed by the mixer were slightly larger than desired but were still quite usable. The pellets were then removed from the mixer and dried, screened (both before and after sintering) and sintered in the same manner as described in Example I with the exception that the sintering temperature used was 1,420° C.

The Stim-Lab conductivity test described in Example I was then performed on the proppant resulting in a conductivity measurement of 5,379 md-ft. after 50 hours at 8,000 psi at 275° F. The dry specific gravity of the proppant was 2.81.

The low density high strength proppant particles of the present invention may be injected into fractures in subsurface formation as a propping agent to increase oil or gas production from the well. In fracturing treatment a viscous fluid, often referred to as a "pad" is injected into the well at extremely high pressure to cause the formation to fail in tension and fracture to accept the fluid. The fracturing fluid may be an oil base, water base, acid, emulsion, foam or other fluid. Normally the fluid contains several additives such as viscosity builders, drag reducers, fluid loss additives, corrosion inhibitors, cross linkers and the like. The fluid of the pad is injected until a fracture of sufficient geometry is obtained to permit the placement of the proppant pellets. Normally the treatment is designed to provide a fracture at the well bore of at least 2 ½ times the diameter of the largest proppant pellet. Once a fracture of the desired geometry is obtained, the proppants are carried suspended in the fluid pad and placed in the fracture. Following placement of the proppant, the well is shut-in for an amount of time sufficient to permit the pressure to bleed off into the formation which in turn causes the fracture to close and exert closure stress on the proppant particles. The shut-in period may vary from a few minutes to several days. The proppant particles of the present invention are particularly suitable for use as propping agents in wells of depths less than about 14,000 feet.

What is claimed is:

1. A low density, high strength proppant comprising solid ceramic pellets consisting essentially of a sintered kaolin clay and having a dry specific gravity of 3.0 or less, said kaolin clay having an alumina content of about 58% or less, said proppant having a conductivity of at least 4,400 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of a deoxygenated aqueous 2% solution of KCl as measured by the Stim-Lab Technique.

2. The proppant of claim 1 wherein said pellets have a specific gravity between 2.65 and 3.0.

3. The proppant of claim 2 wherein the pellets have a specific gravity between 2.65 and 2.85.

4. The proppant of claim 1 wherein said conductivity is at least 5500 md-ft.

5. The proppant of claim 2 wherein said conductivity is at least 5500 md-ft.

6. The proppant of claim 3 wherein said conductivity is at least 5500 md-ft.

7. The proppant of claim 1 wherein said kaolin clay is calcined at a temperature below that which would cause the transformation of any significant portion of said kaolin clay to mullite or crystobalite for a time sufficient to reduce the LOI thereof to 12% or less when tested at 1400° C.

8. The proppant of claim 7 wherein said pellets are produced by adding water to said kaolin clay after calcining while simultaneously mixing and compacting it to form pellets therefrom in a desired size range and drying and sintering said pellets.

9. The proppant of claim 8 wherein said mixing and compacting comprise the steps of:

pelletizing an initial amount of milled, calcined kaolin clay powder by simultaneously mixing and compacting said powder while adding water at a controlled rate, and

adding additional amounts of said powder at a controlled rate while continuing said simultaneous mixing and compacting to form pellets therefrom in a desired size range.

10. The proppant of claim 9 wherein said step of pelletizing further includes dispersing an organic binder in said powder prior to adding water.

11. The proppant of claim 9 wherein the amount of water added is between 32 w/o and 40 w/o of the initial amount of said powder.

12. The proppant of claim 9 wherein the additional amounts of said powder added subsequent to adding said water is between 35 w/o and 50 w/o of the initial amount of said powder.

13. A low density, high strength proppant comprising solid ceramic sintered pellets having a dry specific gravity of 3.0 or less produced by the steps of:

pelletizing a milled, calcined kaolin clay powder which is substantially free of mullite and crystobalite by simultaneously mixing and compacting said powder while adding water at a controlled rate, and adding additional amounts of said powder at a controlled rate while continuing said mixing to form pellets therefrom in a desired size range; and

drying and sintering said pellets.

14. The proppant of claim 13 wherein the pellets have a dry specific gravity of between 2.65 and 2.85.

15. A low density, high strength proppant comprising solid ceramic pellets, said pellets consisting essentially of a sintered kaolin clay having a dry specific gravity of 3.0 or less, said proppant having a conductivity of at least 4,400 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of a deoxygenated aqueous 2% solution of KCl as measured by the Stim-Lab Technique, said kaolin clay having been calcined before compaction at a temperature below that which would cause the transformation of any significant portion of said clay to mullite or crystobalite for a time sufficient to reduce the LOI of said clay to 12% or less when tested at 1400° C.

16. The proppant of claim 15 wherein the dry specific gravity of said pellets is between 2.65 and 2.85.

17. The proppant of claim 15 wherein said conductivity is at least 5,500 md-ft.

18. The proppant of claim 15 wherein said pellets contains less than about 10% of a glassy phase and less than about 2% iron oxide.

19. A low density, high strength proppant comprising solids ceramic pellets consisting essentially of mullite and crystobalite, said pellets containing less than about

10% of a glassy phase, said proppant having a dry specific gravity of 3.0 or less and a conductivity of at least 4,400 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of a deoxygenated aqueous 2% solution of KCl as measured by the Stim-Lab Technique.

20. The proppant of claim 19 wherein said pellets contain between 60 and 80 w/o mullite and between about 15 and 35 w/o crystobalite.

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EXHIBIT 4

United States Patent [19]

Rumpf et al.

[11] **Patent Number: 4,921,821**
[45] **Date of Patent: May 1, 1990**

[54] **LIGHTWEIGHT OIL AND GAS WELL PROPPANTS AND METHODS FOR MAKING AND USING SAME**

[75] Inventors: **David S. Rumpf; Paul R. Lemieux,** both of Ft. Smith, Ark.

[73] Assignee: **Norton-Alcoa Proppants,** Fort Smith, Ark.

[21] Appl. No.: **297,877**

[22] Filed: **Jan. 17, 1989**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 227,258, Aug. 2, 1988, abandoned.

[51] **Int. Cl.^{5}** **C04B 35/10**
[52] **U.S. Cl.** **501/128;** 501/127; 501/133; 501/144; 166/280
[58] **Field of Search** 501/127, 133, 144, 128; 166/280

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[57] **ABSTRACT**

A lightweight oil and gas well proppant made by simultaneously mixing and compacting a milled calcined kaolin clay powder to form green pellets and then drying, screening and sintering the pellets to form proppant pellets having a specific gravity of 3.0 or less and a conductivity of at least 4,200 millidarci-feet and preferably at least 5,100 md-ft as measured by the Stim-Lab method after 50 hours at 8,000 psi and 275° F. in the presence of deoxygenated aqueous 2% solution of KCl.

22 Claims, No Drawings

LIGHTWEIGHT OIL AND GAS WELL PROPPANTS AND METHODS FOR MAKING AND USING SAME

FIELD OF INVENTION

This invention relates generally to lightweight proppants for oil and gas wells and more particularly to lightweight proppants for oil and gas wells having increased strength and conductivity and to methods of making and using such proppants.

BACKGROUND

Hydraulic fracturing is a process of injecting fluids into a selected oil or gas bearing subsurface earth formation tranversed by a well bore at sufficiently high rates and pressures such that the formation fails in tension and fractures to accept the fluid. In order to hold the fracture open once the fracturing pressure is released a propping agent (proppant) is mixed with the fluid which is injected into the formation.

Hydraulic fracturing increases the flow of fluids from an oil or gas reservoir to a well bore in at least three ways: (1) the overall reservoir area in communication with the well bore is increased, (2) the proppant in the fracture generally has significantly higher permeability than that of the formation, thereby allowing fluids to flow more easily, and (3) the high conductivity channel causes large pressure gradients to be created in the reservoir past the tip of the fracture.

Proppants are generally strong, preferably substantially spherical, particulates that should be able to withstand the high temperatures and pressures and corrosive environments experienced in the subsurface formations surrounding an oil or gas well. Early proppants were formed of material such as glass beads, sand, walnut shells and aluminum pellets. These materials did not have sufficient strength or resistance to corrosion to be successful in many wells, particularly where closure pressures above a few thousand psi were experienced.

U.S. Pat. No. 4,068,718 to Cooke relates to a proppant which Cooke states is formed of "sintered bauxite" that has a specific gravity greater than 3.4. Cooke states that specific gravities above 3.4 are required in order that the proppant have sufficient compressive strength to resist fragmentation under the high stress levels experienced in use. While the proppant described in Cooke's example proved to have sufficient strength to resist crushing, the high specific gravity was undesirable since it required the use of higher viscosity fracturing fluids and resulted in a lower volumetric proppant concentration for a given weight of proppant loading in a fracturing fluid when compared with that achieved by a proppant of lower specific gravity. In general, the higher the volumetric concentration of the proppant in the fracturing fluid the wider the propped fracture will be after the fracturing pressure is released.

U.S. Pat. No. 4,427,068 to Fitzgibbon relates to intermediate strength composite proppants made by mixing calcined diaspore clay, burley clay or flint clay with alumina, "bauxite" or mixtures thereof such that the ratio of alumina to silica in the composite mix is between nine to one and one to one. The powdered starting materials are mixed in an Eirich mixer and while the mixing is in progress sufficient water is added to cause formation of composite spherical pellets from the powdered mixture. Fitzgibbon states that the rate of water addition is not critical. The pellets are dried and then

furnaced to sinter the pellets. The sintered pellets have a specific gravity of between 2.7 and 3.4.

U.S. Pat. No. 4,522,731 to Lunghofer relates to an intermediate strength proppant having an alumina content between 40% and 60% which is produced using a spray agglomeration process and which has a density of less than 3.0 gr/cc. In a preferred embodiment Lunghofer produces his proppants from "Eufaula bauxite" which it states is bauxitic-kaolin type material deposited in and around Eufaula, Ala. According to Lunghofer, the Eufaula bauxite preferably contains at least some (above 5%) gibbsite.

U.S. Pat. No. 4,668,645 to Khaund relates to an intermediate strength proppant made from a mined "bauxitic clay" having a specified chemical composition.

The proppants described in the Fitzgibbons, Lunghofer and Khaund patents have specific gravities lower than that of the earlier Cooke proppant and proppants having such lower specific gravities have been used with some success in intermediate depth wells where the stress on the proppant is in the 5,000 to 10,000 psi range. These lower specific gravity proppants, however, all have compressive strengths which are substantially lower than that of high specific gravity materials such as that referred to in the Cooke, et al. patent, which limits the conductivities and permeabilities that are obtained with such proppants, particularly at closure pressures over about 10,000 psi.

The conductivity of a proppant under specific conditions of stress, temperature, corrosive environment and time is the single most important measure of its quality. The conductivity of a packed proppant such as might be deposited in a fracture is defined as the permeability of the proppant pack multiplied by the width of the propped fracture and is usually stated in units of millidarci-feet ("md-ft").

The conductivity of currently available intermediate strength proppants is frequently measured by the tentative API 8 hour procedure, "Tentative Fifth Draft of Recommended Practices For Evaluating Short Term Proppant Pack Conductivity", (Mar. 1987) (hereinafter the "API 8 hour Procedure"), which procedure is hereby incorporated by reference.

Recently a consortium of some twenty-eight organizations involved in various aspects of the fracturing and stimulation business bas sponsored research on ways of evaluating and improving stimulation techniques. Stim-Lab, Inc. of Duncan, Okla. acts as the testing arm of the consortium to develop consistent and repeatable testing procedures for proppants including tests for determining their permeability and conductivity. The long term conductivity testing techniques developed by Stim-Lab have been widely accepted in the industry and are described in a publication of the Society of Petroleum Engineers, No. SPE 16900, entitled "An Evaluation of the Effects of Environmental Conditions and Fracturing Fluids on the Long-Term Conductivity of Proppants" by G. S. Penny of Stim-Lab, Inc., which publication is hereby incorporated by reference. It should be understood that any gap in the description in the SPE publication should be filled in by reference to the API 8 hour Procedure. The testing techniques used by the applicants to determine the conductivity of the proppants of the present invention as they are intended to be supplied to a customer (referred to as the "Stim-Lab Technique") are essentially identical to those described in SPE publication No. 16900 using Monel-K 500 shims in the conductivity cells. A single cell was used rather than stacking 4 cells in the manner described in the SPE publication. This however should have no effect on the measured results. The Stim-Lab Technique is considered to yield conductivity measurements that are repeatable to within about 5–10%.

SUMMARY OF THE INVENTION

In accordance with the invention there is provided a low density, high strength proppant which is formed of solid ceramic particles having a dry specific gravity between 2.65 and 3.0 and preferably between 2.65 and 2.85 and a conductivity of at least about 4000 md-ft and preferably at least 4400 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of a deoxygenated 2% aqueous solution of KCl as measured by the Stim-Lab Technique. Most preferably the conductivity is at least 5500 md-ft as measured under the above conditions.

The proppant of the invention may be produced by milling or other comminuting calcined kaolin clay to an average agglomerated particle size of about 8 microns or less, and preferably of 5 microns or less, and pelletizing said powder in a compacting mixer. The kaolin clay is calcined at a temperature of less than 900° C. to reduce the loss on ignition ("LOI") to 12 w/o or less when tested at 1400° C. Applicants have found in accordance with the invention that it is important that the calcining be done at a low enough temperature that the kaolin clay does not undergo a phase transformation to mullite and crystobalite during such calcining.

Preferably, an organic binder is first dispersed in the milled kaolin clay in the mixer and then water is added to the powder at a controlled rate while mixing and compacting the powder to form rough pellets of a desired size. Next, with the mixer still running, additional dry, milled kaolin clay powder is slowly added to yield smooth, spherical pellets. The pellets are then dried and fired to convert the material to proppant pellets that preferably comprise between about 60 weight percent (hereinafter "w/o") and 85 w/o mullite, between about 15 w/o and 35 w/o crystobalite and a minor amount (less than 10 w/o) of a glassy phase and having a specific gravity of between 2.65 and 3.0.

In accordance with another aspect of the invention, the proppant is mixed with a fluid and injected into a subterranean formation under high pressure to open a fracture, with the proppant remaining in the fracture to prop it open after the fracturing pressure is removed. Surprisingly and unpredictably, the measured conductivities of the proppants of the present invention are up to 100% higher than those of other known intermediate strength proppants, even ones which have higher specific gravities.

DETAILED DESCRIPTION

The preferred raw material for use in making the low specific gravity, high strength proppants of the present invention is kaolin clay. Preferably the kaolin clay consists largely of kaolinite ($Al_2Si_2O_5(OH)_4$) and is essentially free of sand (i.e., quartz). One source of such material is from the American Cyanamid Company in Andersonville, Ga. The Andersonville kaolin deposits owned by American Cyanamid are well described in a report by Alfred D. Zapp entitled "Bauxite Deposits of the Andersonville District, Ga.", U.S. Geological Survey Bulletin 1199-G. This report is incorporated herein by reference. The report states that the deposit consists largely of the mineral kaolinite and is essentially sand free. The chief impurities are compounds of iron and titanium and small amounts of gibbsite. The kaolin clay is deposited in tabular lenticular masses, the thicker of which may have cores of bauxite or bauxitic clay. Raw materials containing significant amounts of sand (free silica or quartz) produce a weaker proppant, while raw materials containing too much gibbsite or other hydrated aluminas yield a product having an undesirably high specific gravity. Another source of material believed to be suitable is the kaolin clay mined at the Mulcoa operations in Andersonville, Ga. of C. E. Minerals, headquartered in King of Prussia, Pa.

In general the kaolin clay most useful as a raw material in making the proppants in accordance with the invention may contain by chemical analysis between about 43 w/o to 58 w/o alumina, about 37 w/o to 52 w/o silica, less than 2 w/o (preferably less than 1 w/o) iron oxide and less than 5 w/o free quartz. Preferably, the kaolin clay comprises between 70 w/o and 90 w/o kaolinite, between 5 w/o and 25 w/o cryptocrystalline to amorphous gibbsite and less than 5 w/o other crystalline materials.

Preferably the amount of free quartz is less than 2 w/o and most preferably is non-detectable. Other naturally occurring minerals which may be present in minor or trace amounts include anatase and rutile. Minerals whose presence in the raw material appear to be somewhat detrimental to the properties of the final product include quartz, pyrite, marcasite, siderite, micas and montmorillonites.

The raw material is preferably calcined before further processing in order to remove water and organics. In accordance with the invention, applicants have found that the calcining should be performed at a temperature low enough that the kaolin clay does not undergo a phase change to form mullite or crystobalite. Applicants have found that the presence of any significant amount of mullite or crystobalite in the kaolin clay before the final drying and firing steps has a severaly detrimental effect on the properties of the proppants produced. Therefore the calcining should be performed at a temperature below 900° C. for a sufficient time that the loss on ignition ("LOI") of the kaolinite is 12 w/o or less when tested at 1400° C. The calcining may be performed relatively quickly at temperatures on the order of 700° to 800° C. or may be performed more slowly at lower temperatures. If the calcining temperature is above about 450° to 500° C., the kaolinite is converted to amorphous alumina and silica (sometimes referred to as "meta kaolinite"). Such a transformation, however, has no adverse effect on the product of the invention.

The calcined material is then reduced in particle size, preferably by dry ball milling in a closed loop system containing a particle classifier. The average agglomerated particle size in this milled material should be about 8 microns or less, and preferably 5 microns or less, as measured by a Sedigraph (Micro Meritics Instrument Corp.) or a Granulometre' (Cilas Compagnie Industrielle des Lasars). The true ultimate particle size, however, of the milled raw material is much finer than 8 or 5 microns and is believed to be made up of submicron flakes. Such submicron flakes tend to agglomerate to form composite particles on the order of 8 microns or less which are sensed by the measuring instruments.

The milled raw material is pelletized in a compacting mixer. The preferred commercially available machines for this purpose are the Eirich Countercurrent Intensive Mixers which are manufactured in several sizes of different capacities by the Maschinenfabrik Gustav Eirich of Hardheim, West Germany and distributed in the U.S. by Eirich Machines, Inc., New York, N.Y.

The Eirich mixer has a rotating mixing pan forming the bottom of the mixing chamber which pan can be either horizontal or inclined at an angle and a "mixing star" which rotates in the opposite direction from the pan. The mixing star rotates about an axis parallel to and offset from that of the pan and has a diameter of about 20 to 25 percent of that of the pan. The preferred form of mixing star for the pelletizing operation is referred to by Eirich as a suction type rotor and has a plurality of vertically extending trapidzoidally shaped mixing elements which extend from the periphery of the rotating element. For the Model R7 machine, the pan has a single rotational speed of about 45 rpm, while the mixing star has a low and a high speed. The low speed is about 700 rpm and the high speed is about twice that, about 1400 rpm. The rotational speeds of the elements of the larger mixers are adjusted so that rotating elements have similar tip speeds. The mixer may also contain a second mixing star upon which can be mounted plows for cleaning the sides of the rotating pan. This second mixing star is also mounted eccentrically in the mixer and rotates in the opposite direction from the mixing pan. An example of another compacting mixer that is believed suitable for use in the present invention is the Littleford Lodige mixer.

The milled, calcined kaolin clay powder charge is preferably first mixed dry in the mixer with about to 2 w/o, (calculated on the basis of the initial kaolin clay powder charge) of an organic binder such as a gelatinized cornstarch for a period of about 30 seconds with the suction rotor on the low speed setting in order to fully disperse the binder in the raw material powder.

It is preferred that such binders be such that they are pyrolized or driven off during later firing of the proppant pellets. The amount of the binder is normally on the order of 1 w/o to 2 w/o of the initial kaolin clay powder charge. It is possible to make pellets with the method of the invention without a binder but it is believed that the use of a binder results in improved properties and yield.

Next water is added at a controlled rate to the mixer with the suction rotor running at the low speed setting to initially pelletize the material. The rate of water addition should be controlled properly to facilitate the formation of the pellets in the mixer and can affect the quality of the final product. Typically the total amount of water for the Model R7 Eirich mixer is from about 32 to 40 w/o of the initial starting material and preferably about 35 to 40 w/o. Preferably between about 40 and 60 w/o of the expected total amount of water is added after the binder is dispersed and mixed for about 2 to 4 minutes. Thereafter additions of about 8 to 10% of the total water are made about every 0.75 to 1.5 minutes until irregularly shaped pellets ranging in size from about ⅛ to ¼ inch in diameter are formed.

Once pellets have formed in the mixer, which at this point are normally large and irregularly shaped, the suction rotor is switched to the high speed setting and additional milled calcined raw material (referred to as "dust") is slowly added to the mixer over a period of about 5 minutes in order to cause the pellets to become smaller, well shaped spheres of a narrower size distribution, typically 0.02 inches to 0.047 inches. Typically, the amount of dust required to form the desired size spheres is about 32 to 50 w/o of the starting raw material. Preferably about 40 to 45 w/o dust is added.

In some cases the suction rotor is switched back to the low speed setting for a later portion of the 5 minute period after a major portion of the dust has been added to the mixer. After adding the dust, the suction rotor is then preferably set back to the low speed setting if it has not already been and the mixer run for a further period of about 30 seconds in order to improve the sphericity of the pellets and to increase yield of the desired size range.

The amount and rate of water and dust additions to the mixer can have a significant impact on the conductivity of the proppant produced by the method of the invention. If too much water is added, the particles are poorly shaped and are too large. If the dust is added too quickly it results in a poor yield of particles in the desired size range. If not enough dust is added the particles are poorly shaped and will stick together in agglomerated masses. If too much dust is added the particles have a rough surface and unconsolidated dust remains in the mixer. When the right amount of dust is added, the process yields smooth, spherical, well compacted pellets. It has been found that mixing times towards the lower end of the above stated time ranges during the addition of water in the mixer tend to yield proppants having conductivities of about up to 30 percent higher than if the mixing times are towards the high end of those ranges.

The spherical pellets are next discharged from the mixer and dried to a free moisture content of less than 10% and preferably less than 5%. The drying temperature and time does not appear to be critical and it has been found, for instance, that drying at temperatures of 150° C. overnight, or of 260° C. for 10 to 15 minutes are suitable. Once dried, the desired size spherical pellets are separated by screening for instance to a 18/35 mesh size. The larger than 18 mesh and finer than 35 mesh are recycled to be repelletized. The screened particles in the desired size range are then sintered, for instance in a rotary kiln, at a temperature between 1300° and 1500° C., preferably between 1400° to 1470° C. for about 15 to 30 minutes at temperature. The total time in the kiln is normally from about 1 to 1½ hours. The particles shrink upon firing by about 15% to 20%. The desired finished size is between 0.0167 inches and 0.0331 inches but can be larger or smaller as needed. The particular temperature to which the screened particles are fired is selected in order to maximize their strength. This temperature depends on several variables, some of which are the raw material mineralogy, the milled particle size, the pellet size and the volume of material in the kiln.

After firing, the pellets are again screened to the desired final size. A typical product size is 20/40 mesh which contains 90 w/o of its pellets of between 0.0167 inches and 0.0331 inches in size and preferably 90 w/o of the pellets between 0.0232 inches and 0.0331 inches in size.

Surprisingly and unexpectedly, it has been found that the proppants of the present invention have conductivities that are up to 100% higher than previously known intermediate strength proppants, even ones of higher specific gravities. The conductivities of the proppants of the preferred embodiment of the present invention are at least 4000 md-ft, and preferably at least 4400 md-ft, after 50 hours at 8000 psi and 275° F. in the presence of a deoxygenated 2% aqueous solution of KCl as measured by the Stim-Lab Technique. Most preferably the conductivity is at least 5500 md-ft when measured under the above conditions. The proppants of the preferred embodiment of the present invention have dry specific gravities of between 2.65 and 3.0 and preferably between 2.65 and 2.85.

For example, one proppant in wide commercial use which is believed to have been made by the method described in the above referred to Lunghofer patent from starting materials which are very similar to those referred to in that patent have been measured in accordance with the Stim-Lab Technique to have conductivities between 3,057 md-ft and 3700 md-ft after 50 hours at 275° F. and 8,000 psi in the presence of a deoxygenated aqueous 2% KCl solution. The proppants of the following Examples of the present invention, on the other hand, have conductivities between about 4080 md-ft and 6,878 md-ft depending on starting materials and processing conditions when measured under the same conditions.

While the reasons for the dramatically higher conductivities of the proppants of the present invention over those of the prior art are not fully understood, it is believed that they may relate in substantial part to a combination of factors such as the mineralogy and microstructure of the proppant pellets and to the fact that the proppant of the present invention is made from a nearly pure kaolinite raw material which has been calcined at low enough temperatures that it is not then converted to mullite and crystobalite and which has been milled to a fine particle size and then formed into pellets with compaction. In contrast, in the technique of the Lunghofer patent, the raw material is not calcined or milled prior to forming the pellets and the fluidized bed technique used to form the pellets does not provide any compaction during formation.

From a mineralogical point of view the sintered pellets of the preferred embodiment of the present invention are between about 60 w/o and 85 w/o mullite and between about 15 w/o and 35 w/o crystobalite and between about 0 w/o and 10 w/o of a glassy phase. It is believed that the glassy phase is best minimized for the highest quality product.

While the measured specific gravity of the above referred to commercially available proppant is slightly lower than the proppants of the present invention to which it was compared (2.70 vs. 2.80 to 2.90, respectively), this slight difference in density does not explain increases in conductivity of up to 100% and more. This is especially so in light of the fact that intermediate strength proppants such as Interprop Plus and Interprop 1 manufactured by the assignee of the present invention which have specific gravities of about 3.17, have been measured by the same technique to have conductivities of 3808 md-ft and 3269 md-ft, respectively. Thus, even though the proppant of the present invention has a specific gravity lower than that of the Interprop Plus and Interprop 1 proppants, its conductivity is up to more than 80% higher than Interprop Plus and 110% higher than Interprop 1. The Interprop Plus and Interprop 1 proppants are made with different raw materials but with a compacting mixer technique.

EXAMPLES

The invention is further illustrated by reference to the following non-limiting examples wherein all percentages are by weight unless otherwise specified. All of the raw materials have been calcined at a temperature of 480° C. for a period of approximately 24 hours to an LOI of between 11.0 and 12.1 when tested at 1400° C., and have been ball milled in a Conical closed circuit ball mill with a gyrotor air classifier manufactured by Mineral Processing Systems, Inc. in York, Pa. Unless otherwise indicated, the pellets are screened to an 18/35 mesh size after drying and to a 20/30 mesh size after sintering wherein 90% of the pellets are between 0.0232 inches and 0.0331 inches in size. The typical yield of properly sized pellets in the first screening is about 70%. The chemical compositions of the calcined kaolin clay powders used as raw materials in Examples 1–4 are summarized in Table I. The mineralogical composition of such raw materials as measured by the X-ray diffraction technique is summarized in Table II. It should be noted that in addition to the components listed in Table II, the raw material powders also contain cryptocrystalline to amorphous gibbsite and perhaps other non-crystalline materials which are not detected by the X-ray diffraction technique. In the components in Table II which divide into major minerals which comprise about 95 w/o of the detected minerals present and the minor minerals which together make up less then 5 w/o of the detected minerals present. The amount of gibbsite present can be determined from Table II since in all but Example 3 the amount of SiO_2 present as free quartz is non-detectable so that any Al_2O_3 present which is not part of the kaolinite is believed to be in the form of cryptocrystalline to amorphous gibbsite. Kaolinite is approximately 45 w/o Al_2O_3.

TABLE I

Example	1	2	3	4
Chemistry				
Al_2O_3	57.14	57.14	48.76	49.29
SiO_2	38.66	38.66	47.76	48.70
Fe_2O_3	1.19	1.19	.94	.90
TiO_2	2.82	2.82	2.18	1.95
CaO	.08	.08	.07	.03
MgO	.03	.03	.03	.03
Na_2O	.04	.04	.12	.04
K_2O	.04	.04	.14	.06

TABLE II

Example	1	2	3	4
Mineralogy				
Major Minerals				
Kaolinite	Major	Major	Major	Major
Quartz	ND	ND	Minor	ND
Gamma Fe_2O_3	ND	ND	ND	Trace
Minor Minerals				
Anatase	Major	Major	Trace	Minor
Rutile	Trace	Trace	Trace	O

Where "ND" means non-detectable

EXAMPLE I

A 50 lb. charge of milled, calcined kaolin clay obtained from the American Cyanamid, Andersonville, Ga. deposits and having the chemical and mineralogical composition indicated in Tables I and II was placed in an Eirich Model R7 Compacting Mixer having an inclined pan and a suction type rotor along with 1 lb. of gelatinized cornstarch binder and mixed for 30 seconds with the suction rotor in its low speed setting in order to fully disperse the binder in the kaolin clay powder. With the suction rotor rotating at its low speed setting, 9 lbs. of water was added to the mixer and mixed for a period of two minutes. As the suction rotor continued to operate in the low speed setting, four 2 lb. additions, followed by two 1 lb. additions and a ½ lb. addition of water were added sequentially to the mixer with a 45 second mixing period after each addition. At this point irregularly shaped pellets had formed.

The rotor was then switched to the high speed setting and an additional 12 lbs. of the same milled, calcined kaolin clay powder was slowly added to the mixer over a three minute period. Then the rotor was reset to its low speed setting and additional 6 lbs. of the kaolin clay powder was added over a period of two minutes. The mixing was continued with the suction rotor in the low speed setting for an additional period of 30 seconds. At this point the particles had fairly good sphericity but had rather rough surfaces. An additional 2½ lbs. of the kaolin clay powder were slowly added to the mixer over a 1 minute period and the material mixed for an additional 30 seconds with the suction rotor continuing in the low speed setting. The pellets now had a good spherical shape and smooth surfaces. The pellets were discharged from the mixer and dried overnight at 150° C. in a box oven. After drying the pellets were screened to an 18/35 mesh and fired at 1470° C. in a rotary kiln for a period of about 30 minutes at temperature with a total time in the kiln of approximately 1 hour 15 minutes. After cooling the pellets were screened to a 20/30 mesh. The dry specific gravity of the material was 2.90 as measured by a Beckman air comparison pycnometer Model 930.

A conductivity test using the Stim-Lab Technique referred to above was conducted with final closure stress of 8,000 psi at 275° F. in the presence a deoxygenated aqueous 2% solution of KCl for 50 hours. In accordance with this procedure 63.06 grams of the screened proppant pellets were loaded into a API Hasteloy-C 10 in^2 linear flow cell to give a loading of 2 lbs./ft^2 of proppant and leveled loosely with a universal bevel blade device. A 0.030" thick Monel shim was placed on top of the test pack followed by an O ring fitted to a piston which was lightly coated with vacuum grease. The loaded test cell was then placed in a 150 ton Dake press and the closure stress was increased to 500 psi at a rate of 100 psi/min. The cell was saturated with deoxygenated aqueous 2 w/o KCl solution and then purged of air at the ambient laboratory temperature of 70° F. to 80° F. A Validyne DP15-30 differential pressure transducer connected across the cell was calibrated with water columns to 0.0001 psi accuracy. Closure stress was then raised to 1,000 psi at a rate of 100 psi/min. A Reservoir Accumulator, made up of two 5 gal and two 1 gal nitrogen driven fluid reservoir accumulators which were filled with a 2 w/o KCl aqueous solution that had been deoxygenated with nitrogen to a level of less than 15 ppb and preferably less than 5 ppb of oxygen was connected to the test cell and set at a driving pressure of 400 psi. The connection of the Reservoir Accumulator to the cell is make through two 150 ml sample cylinders filled with 100 mesh Oklahoma #1 sand with ceramic band heaters in order to saturate the test fluid with silica. It should be noted that the closure stresses on the proppant pack in the cell are stated in terms of the net closure stress on the pack which is equal to the gross pressure applied by the press minus the 400 psi pressure applied by the reservoir accumulator.

The system was allowed 30 minutes to come to equilibrium and a series of five conductivity measurements were taken and averaged. The conductivity was calculated from the darci relationship:

$$k_{wf} = 26.78\ \mu Q/P$$

where

k_{wf} = Conductivity (md-ft)

26.78 = factor to account for a 1½×5 inch flow area and pressure in psi

μ = Viscosity of flowing fluid at temperature (cp)

Q = Flow rate (ml/min)

P = Pressure differential across 5 inch flow path.

After the readings were taken at ambient temperature, the temperature was increased to 275° F. and held for 8 hours for temperature uniformity. Next readings with the system at 275° F. were taken at 1,000 psi, 2,000 psi, 4,000 psi, 6,000 psi and 8,000 psi with the closure stress being raised between levels at a rate of 100 psi/min. After reaching each of the 1,000, 2,000, 4,000 and 6,000 closure stress levels, the system was held at 275° F. for 1.5 hours before the conductivity readings were taken. At the 8,000 psi level the cell was held at 275° F. for 50 hours during which conductivity measurements were taken at 10 hour intervals. The measured conductivity at the 50 hour time was 6,247 md-ft.

EXAMPLE II

The same Stim-Lab conductivity test procedure described in Example I was repeated on proppant particles made in Example I. This time the measured conductivity at the 50 hour time was 6,878 md-ft.

EXAMPLE III

In this example kaolin clay, designated as SR105 Sardis, obtained from Alcoa Corporation and having the chemical and mineralogical composition indicated in Tables I and II was utilized. A 50 lb. charge of milled, calcined kaolin clay was placed in the Eirich Model R7 Compacting Mixer described in Example I along with 1 lb. of cornstarch binder and mixed dry for 30 seconds at the low speed setting. Water was then added to the mixer with the mixer operating at the low speed setting with 9 lbs. being added and mixed for 4 minutes followed by 4 additions of 2 lbs. each and a final addition of ½ lb., with 1.5 minute mixing period after each addition.

The mixer was then set to the high speed mode and 11 lbs. of the same milled, calcined kaolin clay powder was slowly added to the mixer over a 3 minute period. The mixer was then switched back to the low speed setting and an additional 7 lbs. of the same kaolin clay powder was slowly added over a 2 minute period, followed by a 30 second low speed mixing. An additional 3½ lbs. of the same kaolin clay powder was added over the following minute followed by an additional 30 second mixing period at the low speed. Then a final 3 lbs. of the kaolin clay powder was added over the following minute. The particles were thereafter discharged from the mixer and screened, dried and fired in the same manner as described in Example I with the exception that the sintering temperature was 1420° C. After cooling the pellets were screened to a 20–30 mesh size. The dry specific gravity of the material was 2.80. The Stim-Lab conductivity test described in connection with Example I was then performed yielding a measured conductivity after 50 hours at 8,000 psi and 275° F. of 4,080 md/ft.

EXAMPLE IV

A 50 lb. charge of milled, calcined kaolin clay obtained from the American Cyanamid Andersonville, Ga. deposits having the chemical and mineralogical composition indicated in Tables I and II was placed in the Eirich Model R7 Compacting Mixer described in Example I along with 1 lb. of the cornstarch binder and mixed with water in the same manner as described in Example I with the exception that the final ½ lb. addition of water was eliminated so that only 19 lbs. of water was added to the mixer. At that point the powder had formed into slightly wet looking somewhat irregularly shaped pellets.

Next the mixer was switched to the high speed setting and 15 lbs. of the same milled, calcined kaolin clay powder was slowly added over a 3 minute period. Next the mixer was switched back to the low speed setting and an additional 7½ lbs. of the kaolin clay powder was added over the following 2 minutes after which the mixer continued to be operated for an additional 30 second period. The pellets formed by the mixer were slightly larger than desired but were still quite usable. The pellets were then removed from the mixer and dried, screened (both before and after sintering) and sintered in the same manner as described in Example I with the exception that the sintering temperature used was 1,420° C.

The Stim-Lab conductivity test described in Example I was then performed on the proppant resulting in a conductivity measurement of 5,379 md-ft. after 50 hours at 8,000 psi at 275° F. The dry specific gravity of the proppant was 2.81.

In accordance with the method of the present invention the low density high strength proppant particles of the present invention may be injected into fractures in subsurface formation as a propping agent to increase oil or gas production from the well. In fracturing treatment a viscous fluid, often referred to as a "pad" is injected into the well at extremely high pressure to cause the formation to fail in tension and fracture to accept the fluid. The fracturing fluid may be an oil base, water base, acid, emulsion, foam or other fluid. Normally the fluid contains several additives such as viscosity builders, drag reducers, fluid loss additives, corrosion inhibitors, cross linkers and the like. The fluid of the pad is injected until a fracture of sufficient geometry is obtained to permit the placement of the proppant pellets. Normally the treatment is designed to provide a fracture at the well bore of at least 2½ times the diameter of the largest proppant pellet. Once a fracture of the desired geometry is obtained, the proppants are carried suspended in the fluid pad and placed in the fracture. Following placement of the proppant, the well is shut-in for an amount of time sufficient to permit the pressure to bleed off into the formation which in turn causes the fracture to close and exert closure stress on the proppant particles. The shut-in period may vary from a few minutes to several days. The proppant particles of the present invention are particularly suitable for use as propping agents in wells of depths less than about 14,000 feet.

What is claimed is:

1. A method for making a low density, high strength proppant comprising the steps of:

pelletizing a comminuted powder consisting essentially of kaolin clay by simultaneously mixing and compacting said powder while adding water at a controlled rate and adding additional amounts of said powder while continuing said simultaneous mixing and compacting, to form pellets in a selected size range; and

drying and sintering said pellets to form proppant particles having a dry specific gravity of 3.0 or less.

2. The method of claim 1 further including the step of calcining said kaolin clay prior to pelletizing at a temperature sufficiently low that the kaolin clay is not converted to mullite or crystohalite.

3. The method of claim 2 further including dispersing an organic binder in said powder prior to the addition of water.

4. The method of claim 2 wherein said pellets have a conductivity of at least 4,000 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of a deoxygenated aqueous 2% solution of KCl, as measured by the Stim-Lab Technique.

5. The method of claim 2 wherein said conductivity is at least 5500 md-ft.

6. The method of claim 1 further comprising screening said pellets to obtain sintered pellets in a desired size range.

7. A method for making a low density high strength proppant comprising the steps of:

calcining kaolin clay under conditions which prevent the transformation of such kaolin clay to mullite or crystobalite;

comminuting said calcined kaolin clay to a powder;

pelletizing said powder by adding water thereto and simultaneously mixing and compacting it to form pellets in a desired size range; and

drying and sintering said pellets.

8. The method of claim 7 wherein said pellets have a dry specific gravity of 3 or less.

9. The method of claim 7 wherein said step of pelletizing further comprises the step of pelletizing an initial amount of said powder while adding water at a controlled rate in an amount from between 32 w/o to 40 w/o of said powder and adding additional amounts of said powder while continuing said simultaneous mixing and compacting to form pellets in a selected size range.

10. The method of claim 9 wherein said step of pelletizing further comprises dispersing an organic binder in said initial amount of kaolin clay powder prior to the addition of said water.

11. The method of claim 10 wherein said step of pelletizing includes:

adding between 40 w/o to 60 w/o of the total amount of water after dispersing said binder and simultaneously mixing and compacting for an initial period; and

adding additional increments of water periodically while continuing said simultaneous mixing and compacting.

12. The method of claim 9 wherein said additional amount of said powder is between about 32 w/o to 50 w/o of the initial amount of kaolin clay powder.

13. The method of claim 7 further comprising the step of screening said pellets to obtain sintered pellets in a desired size range.

14. The method of claim 13 wherein said step of screening includes screening said pellets prior to drying and sintering and further including the step of recycling the pellets falling outside the size range selected by said screening.

15. The method of claim 7 wherein said kaolin clay is calcined at a temperature of less than 900° C.

16. The method of claim 15 where said kaolin clay is calcined to an LOI of 12 w/o or less when tested at 1400° C.

17. The method of claim 9 wherein said step of comminuting includes milling said kaolin clay to an agglomerated particle size of 8 microns or less.

18. The method of claim 16 wherein said kaolin clay is mostly kaolinite.

19. A method for making a low density, high strength proppant comprising the steps of:

calcining a clay material containing alumina and silica and less than about 2 w/o iron oxide and about 5 w/o free quartz under conditions which prevent the transformation of such clay material to mullite and crystobalite;

comminuting said calcined clay material to a powder;

pelletizing said powder by adding water thereto, and forming pellets in a desired size range; and

drying and sintering said pellets.

20. The method of claim 19 wherein said pellets have a specific gravity of 3.0 or less.

21. The method of claim 19 wherein said pellets have a conductivity of at least 4,000 md-ft after 50 hours at 8,000 psi and 275° F. in the presence of a deoxygenated aqueous 2% solution of KCl, as measured by the Stim-Lab Technique.

22. The method of claim 19 wherein said clay material contains between about 43 w/o and about 58 w/o alumina.

23. The method of claim 22 wherein said clay material contains less than 2 w/o free quartz.

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EXHIBIT 5

US005120455A

United States Patent [19]

Lunghofer

[11] **Patent Number: 5,120,455**

[45] **Date of Patent: Jun. 9, 1992**

[54] **HYDRAULIC FRACTURING PROPPING AGENT**

[75] Inventor: **Eugene P. Lunghofer**, Youngstown, N.Y.

[73] Assignees: **Carbo Ceramics Inc.; A/S Niro Atomizer**, both of Irving, Tex.

[21] Appl. No.: **622,542**

[22] Filed: **Dec. 5, 1990**

Related U.S. Application Data

[60] Continuation of Ser. No. 613,032, May 22, 1984, abandoned, Division of Ser. No. 437,206, Oct. 28, 1982, Pat. No. 4,522,731.

[51] **Int. Cl.**^{5} **E21B 43/267**

[52] **U.S. Cl.** **252/8.551**; 166/280; 166/307; 166/308; 51/298; 51/307; 51/309

[58] **Field of Search** .... 252/8.551; 166/280, 166/307, 308; 51/298, 307, 309, DIG. 30

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[57] **ABSTRACT**

A high strength propping agent for use in hydraulic fracturing of subterranean formations comprising solid, spherical particles having an alumina content of between 40 and 60%, a density of less than 3.0 gm/cc and an ambient temperature permeability of 100,000 or more millidarcies at 10,000 psi.

28 Claims, 5 Drawing Sheets

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FIG. 1

PERMEABILITY VS. CLOSURE STRESS COMPARISON

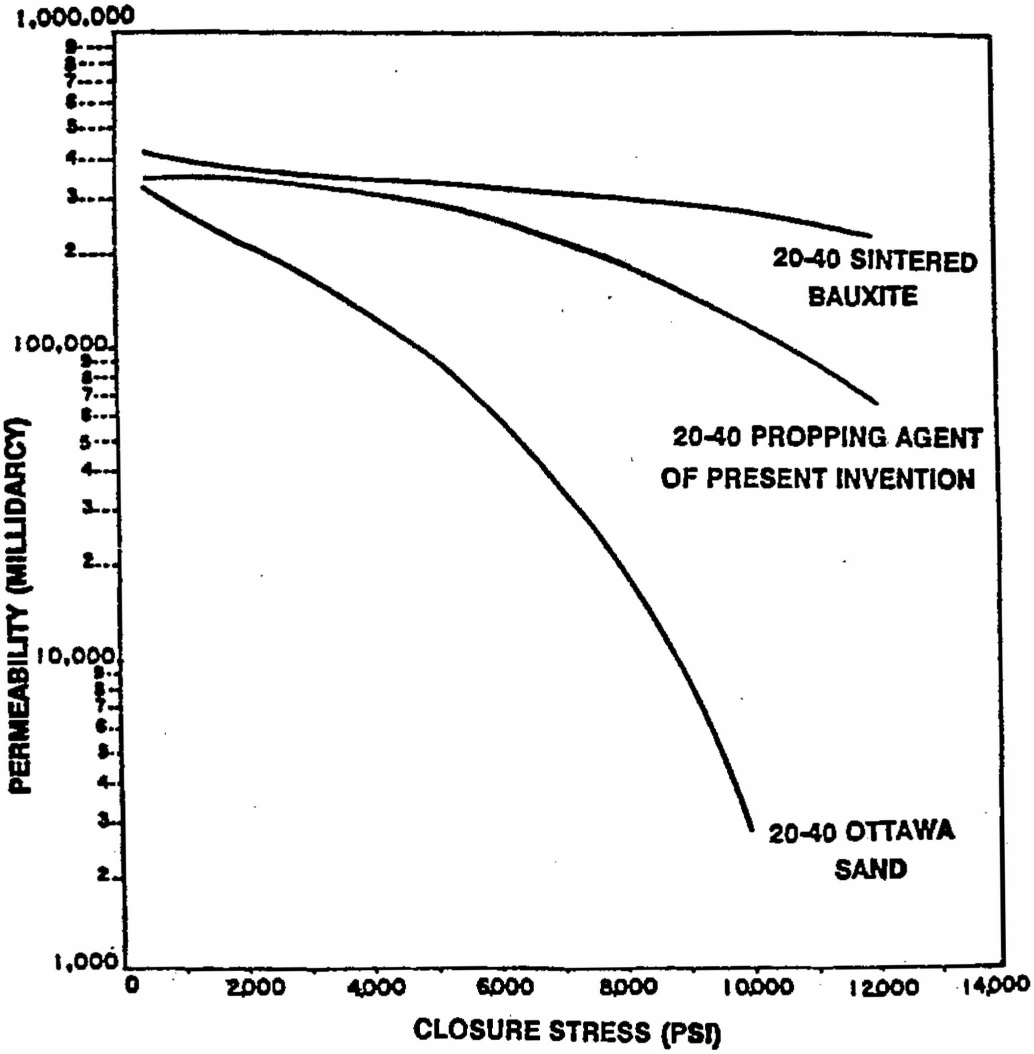


FIG. 2

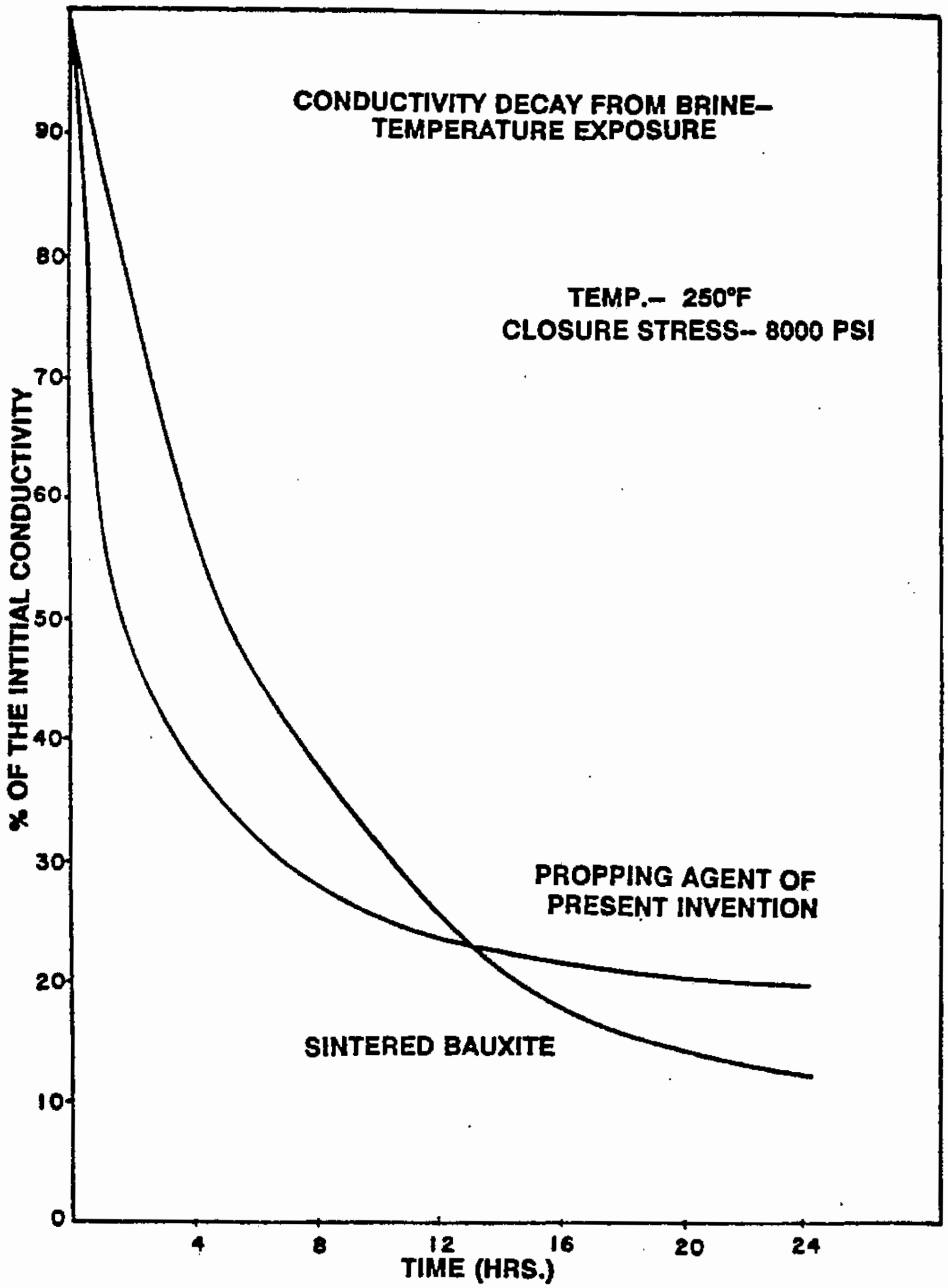

CONDUCTIVITY DECAY FROM BRINE–TEMPERATURE EXPOSURE
TEMP.– 250°F
CLOSURE STRESS– 8000 PSI
PROPPING AGENT OF PRESENT INVENTION
SINTERED BAUXITE
% OF THE INTITIAL CONDUCTIVITY
0
10
20
30
40
50
60
70
80
90
4
8
12
16
20
24
TIME (HRS.)

FIG. 3

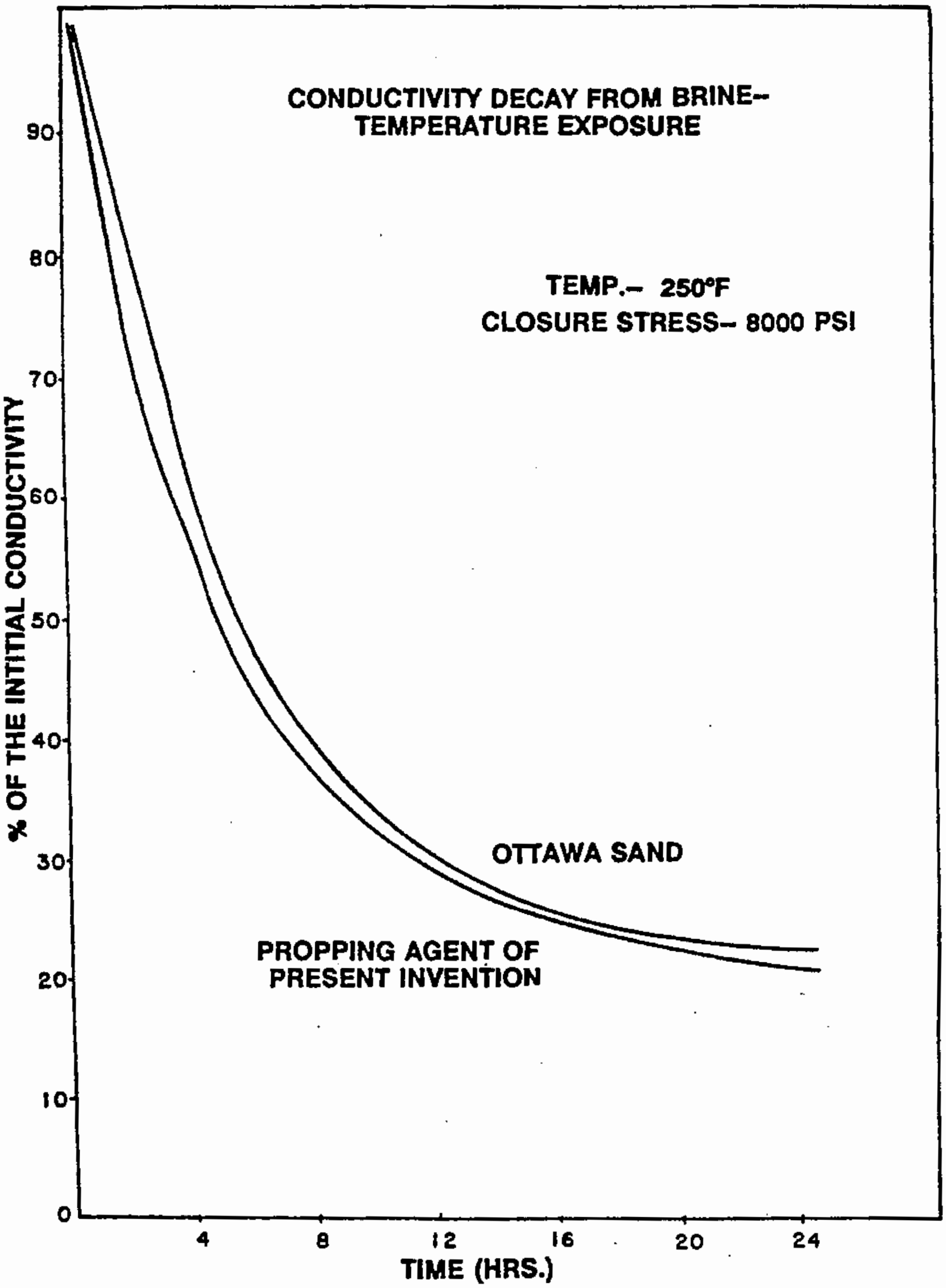

CONDUCTIVITY DECAY FROM BRINE-TEMPERATURE EXPOSURE
TEMP.- 250°F
CLOSURE STRESS- 8000 PSI
OTTAWA SAND
PROPPING AGENT OF PRESENT INVENTION
% OF THE INTITIAL CONDUCTIVITY
0
10
20
30
40
50
60
70
80
90
4
8
12
16
20
24
TIME (HRS.)

FIG. 4

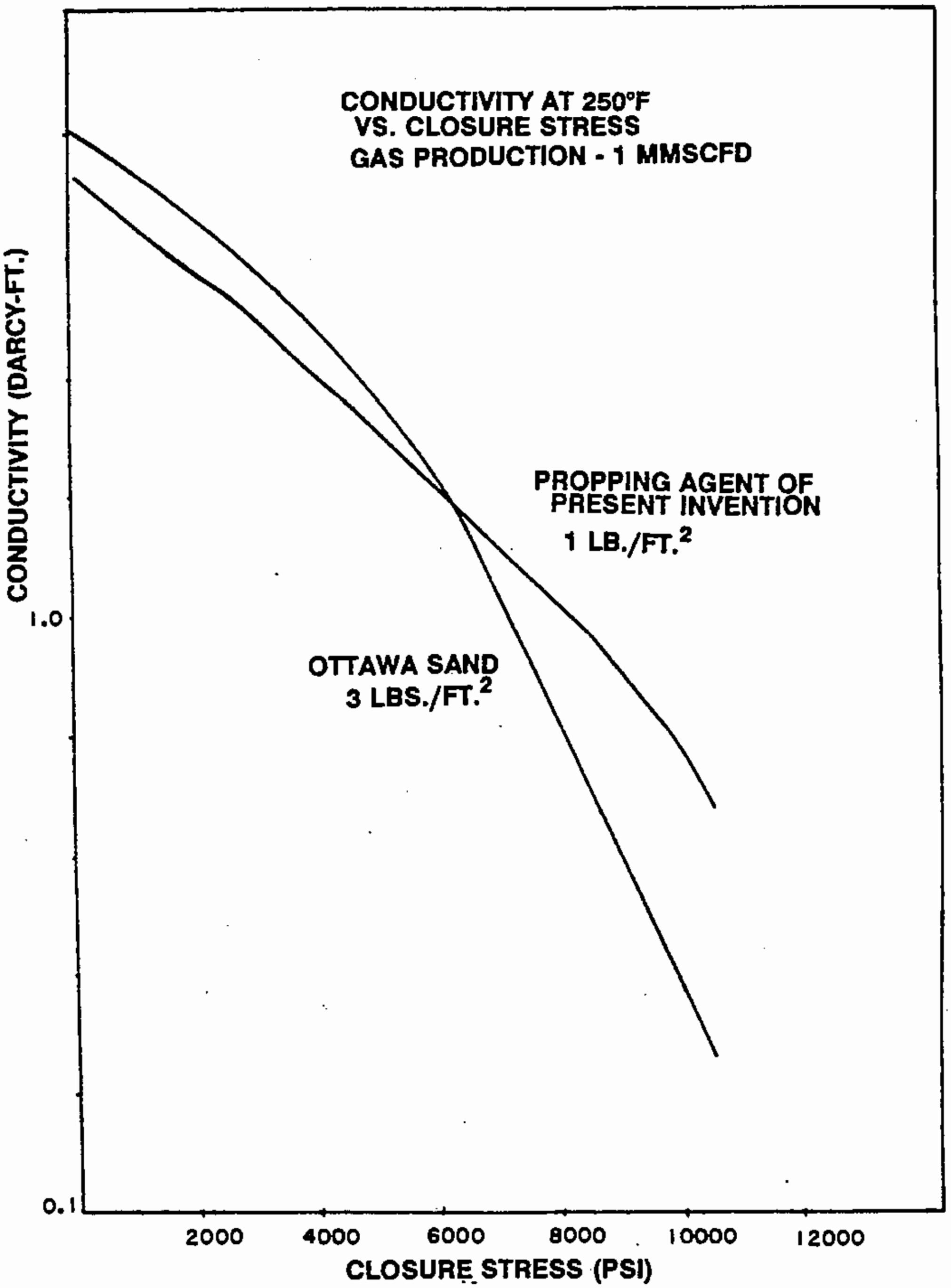
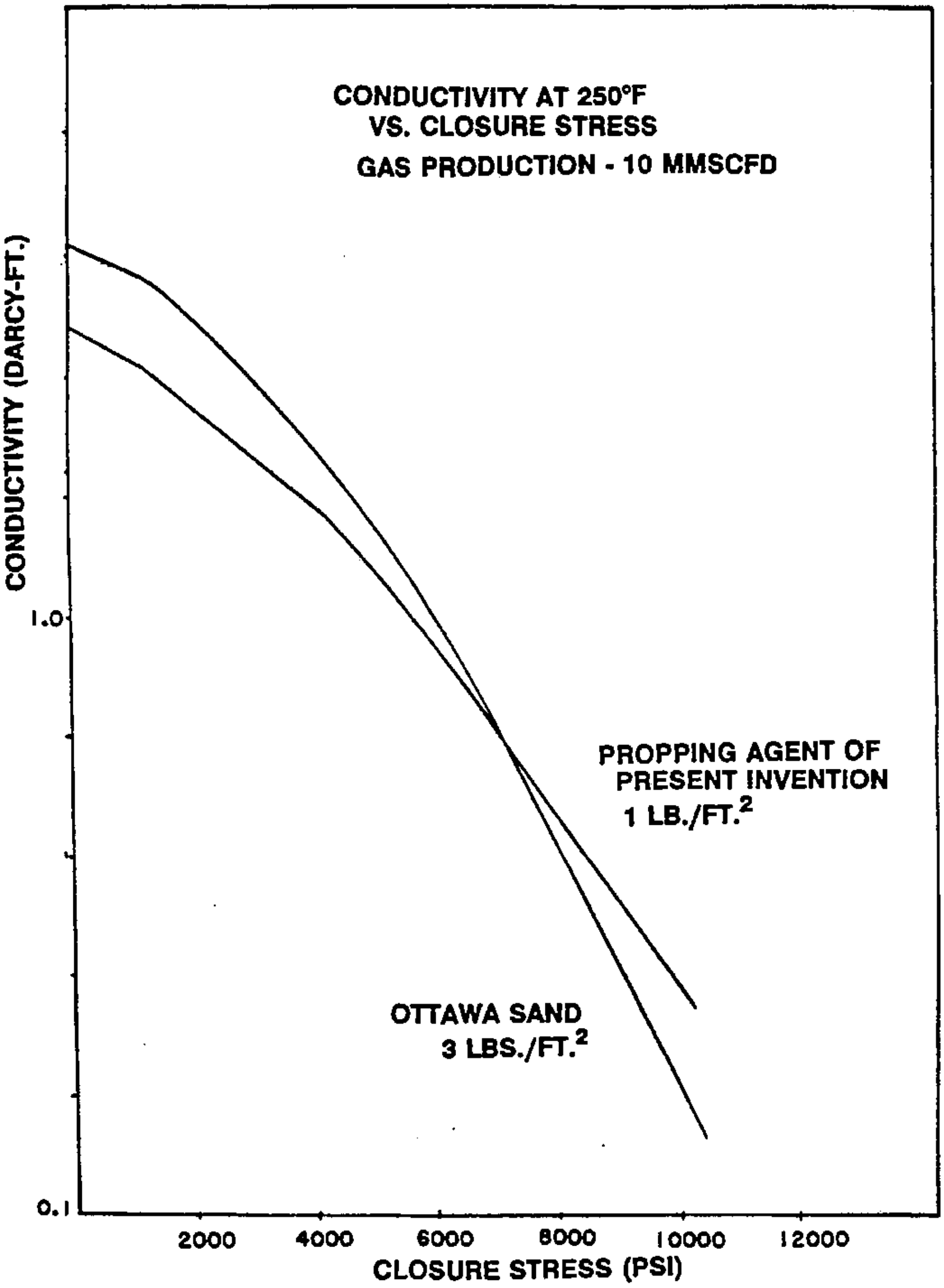

CONDUCTIVITY AT 250°F
VS. CLOSURE STRESS
GAS PRODUCTION - 1 MMSCFD
PROPPING AGENT OF PRESENT INVENTION 1 LB./FT.²
OTTAWA SAND 3 LBS./FT.²
CONDUCTIVITY (DARCY-FT.)
1.0
0.1
2000
4000
6000
8000
10000
12000
CLOSURE STRESS (PSI)

FIG. 5


CONDUCTIVITY AT 250°F
VS. CLOSURE STRESS
GAS PRODUCTION - 10 MMSCFD
CONDUCTIVITY (DARCY-FT.)
1.0
0.1
PROPPING AGENT OF
PRESENT INVENTION
1 LB./FT.2
OTTAWA SAND
3 LBS./FT.2
2000
4000
6000
8000
10000
12000
CLOSURE STRESS (PSI)

HYDRAULIC FRACTURING PROPPING AGENT

This is a continuation of application Ser. No. 613,032 filed May 22, 1984, now abandoned, which is a division of application Ser. No. 437,206 filed Oct. 28, 1982, now U.S. Pat. No. 4,522,731.

BACKGROUND OF THE INVENTION

The present invention relates to propping agents for use in hydraulic fracturing of subterranean formations surrounding oil wells, gas wells, and similar boreholes.

Hydraulic fracturing is a well stimulation technique designed to increase the productivity of a well by creating highly conductive fractures or channels in the producing formation surrounding the well. The process normally involves two steps. First a fluid is injected into the well at a sufficient rate and pressure to rupture the formation thereby creating a crack (fracture) in the reservoir rock. Thereafter a particulate material (propping agent) is placed into the formation to "prop" open the fracture.

In order for well stimulation to occur, the propping agent must have sufficient mechanical strength to withstand the closure stresses exerted by the earth. If the propping agent is not strong enough to resist the earth's closure stresses, then the propping agent will tend to disintegrate thereby reducing the permeability of the propped fracture.

On the other hand, the propping agent must also be inexpensive since large volumes of propping agent are used in a well stimulation treatment. For example, it takes 135,520 pounds of sintered bauxite propping agent to fill a 968 ft^3 fracture. McDaniel et al., "The Effect of Various Proppants and Proppant Mixtures on Fracture Permeability," SOCIETY OF PETROLEUM ENGINEERS OF AIME, AIME Paper No. SPE 7573 (1978) at p. 4 (McDaniel et al.)

Because of its low cost, relative abundance and low density sand is the ideal propping agent for hydraulic fracturing of low closure stress (4,000 psi or less) formations. While specially screened (usually 20–40 mesh) high grade sand (e.g., Ottawa sand) can be used with higher closure stress formations, performance drops off drastically as stress increases, particularly above 8,000 psi. At stresses of 10,000 psi and above even the highest grade sand is inadequate.

Heretofore, the only propping agents known to be able to withstand closure pressures of 10,000 psi or greater was a high density sintered bauxite propping agent. Cooke, "Hydraulic Fracturing with a High-Strength Proppant", SOCIETY OF PETROLEUM ENGINEERS OF AIME, AIME Paper No. SPE 6213 (1976); Jones et al., "Light Weight Proppants for Deep Gas Well Stimulation", submitted to Bartlesville Energy Technology Center by Terra Tek, Inc., under Government Contract #DE-AC19-79BC10038 (June 1980) (Terra Tek paper); McDaniel et al. Described in U.S. Pat. No. 4,068,718 (Cooke et al.), this high strength propping agent consists of sintered bauxite particles having a specific gravity greater than 3.4. High density is described as a critical feature of this propping agent. According to Cooke et al., the high density is necessary to attain high strength and resist fragmentation under high stress levels. They explain that permeability drops off significantly when low density particles (specific gravity below 3.4) are used. (Col. 6, lines 6–35.)

High grade alumina propping agents were also reported to be able to withstand closure pressures of 10,000 psi in U.S. Pat. No. 3,976,138 (Colpoys et al.). This, however, has not been confirmed by independent investigators. In any event, the Colpoys et al. propping agent also consists of high density particles, i.e., specific gravities of 3.40 and greater. Although Colpoys et al. describe a lower density low grade alumina propping agent as well, they do not report that this less preferred propping agent is able to withstand such severe conditions.

While the sintered bauxite propping agent is advantageous in that it can withstand closure pressures of 10,000 psi or greater, there are certain disadvantages associated with its use. On account of its high-density, it requires high viscosity fracturing fluids and/or high pumping rates along with low proppant concentration. This makes fracture control and high conductivity fractures more difficult to obtain. (See Terra Tek paper at p. 3.) Since the Colpoys et al. propping agent has a similar high density, the same problems would be expected to be associated with its use. Additionally, sintered bauxite is relatively expensive. The cost per pound of bauxite is ten to fifteen times that of sand. (See Terra Tek paper at pp. 2–3 and McDaniel et al. at p. 4.) Accordingly, there has been a definite need for a lower density and less expensive propping agent having the mechanical strength to withstand closure pressures of 10,000 psi or greater.

SUMMARY OF THE INVENTION

It is, therefore, a main object of the present invention to provide a propping agent for hydraulic fracturing of subterranean formations which overcomes the above-mentioned drawbacks.

It is a more specific object of the present invention to provide a propping agent for hydraulic fracturing of subterranean formations which has sufficient mechanical strength to be able to withstand closure pressures of 10,000 psi or greater but also has a density of less than 3.0 gm/cc.

A further object of this invention is to provide a propping agent for use in hydraulic fracturing of subterranean formations which is less expensive than sintered bauxite propping agent.

Another object of this invention is to provide a propping agent for use in hydraulic fracturing of subterranean formations which requires lower viscosity fracturing fluids and lower pumping rates than sintered bauxite propping agent.

A still further object of this invention is to provide a propping agent for hydraulic fracturing of subterranean formations which facilitates fracture control and the obtaining of high conductivity fractures.

An additional object of this invention is to provide an economical alternative to sand for medium closure stress (6,000–10,000 psi) subterranean formations.

Additional objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of instrumentalities and combinations particularly pointed out in the appended claims.

To achieve the objects, and in accordance with the purpose of the invention, as embodied and broadly described herein, the invention comprises a high-strength propping agent for use in hydraulic fracturing of subterranean formations comprising solid spherical particles, the particles having an alumina content of between 40 and 60%, a density of less than 3.0 gm/cc, and an ambient temperature permeability of 100,000 or more millidarcies at 10,000 psi.

To further achieve the objects in accordance with the purpose of the invention as embodied and broadly described herein, the invention comprises a hydraulic fracturing method in which a fluid is injected into a subterranean formation to open a fracture therein and a propping agent is placed in the formation to prop open the fracture, the propping agent being solid, spherical particles having an alumina content of between 40 and 60%, a density of less than 3.0 gm/cc, and an ambient temperature permeability of a 100,000 or more millidarcies at 10,000 psi.

The foregoing and other objects, features, and advantages of the present invention will be made more apparent from the following description of the preferred embodiment.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot of permeability versus closure stress for samples of sintered bauxite, Ottawa sand and the propping agent of the present invention tested under laboratory conditions.

FIG. 2 is a plot of conductivity decay from brine and high temperature exposure versus time for samples of sintered bauxite and the propping agent of the present invention tested under laboratory conditions.

FIG. 3 is a plot of conductivity decay from brine and high temperature exposure versus time for samples of Ottawa sand and the propping agent of the present invention tested under laboratory conditions.

FIG. 4 is a plot of conductivity versus closure stress at a flow rate of 1 Mscf/D for a concentration of 1 lb/ft^2 of the Propping agent of the present invention and a concentration of 3 lb/ft^2 of Ottawa sand tested under laboratory conditions.

FIG. 5 is a plot of conductivity versus closure stress at a flow rate of 10 Mscf/D for a concentration of 1 lb/ft^2 of the propping agent of the present invention and a concentration of 3 lb/ft^2 of Ottawa sand tested under laboratory conditions.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference will now be made in detail to the present preferred embodiments of the invention.

A high strength propping agent for use in hydraulic fracturing of subterranean formations surrounding oil wells, gas wells and similar boreholes in accordance with the present invention comprises solid, spherical particles having an alumina content of between 40 and 60%, a density of less than 3.0 gm/cc, and an ambient temperature permeability of 100,000 or more millidarcies at 10,000 psi.

For purposes of the present invention the propping agent particles should have an alumina (Al_2O_3) content of between 40 and 60%, preferably between 45.5 and 60%, and a silica (SiO_2) content of between 36.5 and 56.5%, preferably between 36.5 and 51%. Good results have been obtained with material having the following composition (calcined basis):

SiO_2	45.8
Al_2O_3	50.7
TiO_2	2.60
Fe_2O_3	0.70
CaO	0.03
MgO	0.04
Na_2O	0.06
K_2O	0.05
Li_2O	0.02
Total	100.00

This material had a density of about 2.62–2.65 gm/cc.

In a preferred embodiment, the propping agent particles are made from Eufaula bauxite. The term "Eufaula bauxite" refers to a bauxitic-kaolin type material deposited in and around Eufaula, Alabama. See Burst, J. F., "Genetic Relationship of the Andersonville, Ga. and Eufaula, Ala. Bauxitic-Kaolin Areas", Society of Mining Engineers, *AIME Transactions*, Vol. 246, pp. 137–144 (June 1974), which is incorporated by reference herein as background information. Preferably, the Eufaula bauxite will contain at least some (above 5%) gibbsite. The greater the gibbsite content the higher the loss on ignition. Preferably the loss on ignition will be between 14.5 and 20%. Good results have been obtained with a gibbsite content yielding a loss on ignition of about 17.1%.

A small amount (up to 5%) of the Eufaula bauxite may be replaced with a crush strength enhancer selected from the group: nepheline syenite, fused bauxite dust, wollastonite, talc, and feldspar. Of these, nepheline syenite is the preferred crush strength enhancer. It is believed that addition of up to 5% of one of these crush strength enhancers will serve to impede cristobalite formation upon sintering of the raw material and thereby enhance the crushing strength of the final particles.

The propping agent particles of the present invention may be made by the methods disclosed in copending U.S. Patent application No. 437,321 of Eugene Paul Lunghofer, Sten Mortensen, and Aubrey Ward, filed concurrently herewith on Oct. 28, 1982 for A Process For The Production Of Sintered Bauxite Spheres, now U.S. Pat. No. 4,440,866. As explained therein, an aqueous feed suspension comprising the bauxitic-kaolin type material and a suitable binder is prepared. The feed suspension is then continuously atomized into a layer of already partly dried particles fluidized in a stream of drying air. Particles are continually recovered from this layer and continuously separated into oversized, undersized, and product fractions, making allowance for anticipated shrinkage in the subsequent sintering operation. Undersized fractions, relatively fine product fractions, ground product fractions, and ground oversized product fractions are continuously recycled to the layer of fluidized particles at a substantial distance (measured along the flow path of the particles) from the site where the recovery of such particles takes place. The non-recycled product fractions are dried and sintered by heating at a temperature of between 1200° and 1650° C.

Propping agents made from the above-described materials and by the above-described methods will have a density of less than 3.0 gm/cc, thus, overcoming the disadvantages associated with the high-density sintered bauxite propping agent described above. In a preferred embodiment, the propping agent of the present invention has a Krum being sphericity of about 0.9 or greater. Preferably, 90 percent or more of the propping agent particles of the present invention are 30–40 mesh. Moreover, contrary to the teachings of Cooke et al., the lower density propping agent of the present invention has sufficient mechanical strength to withstand closure stresses of 10,000 psi or greater. The suitability of the propping agents of the present invention for such high closure stress applications is demonstrated by the comparative permeability testing described in Example 1.

EXAMPLE I

Permeability

The permeability of a 20–40 mesh sample of the propping agent of the present invention was compared to a 20–40 mesh sample of sintered bauxite propping agent of the type described by Cooke et al. The propping agent of the present invention had the following composition (calcined basis):

SiO_2	45.80
Al_2O_3	50.70
TiO_2	2.60
Fe_2O_3	0.70
CaO	0.03
MgO	0.04
Na_2O	0.06
K_2O	0.05
Li_2O	0.02
Total	100.00

It had a density of about 2.62–2.65 gm/cc. The sintered bauxite propping agent was a commercial product obtained from The Norton Company. It had an alumina content of between 86 and 89% and a density of about 3.68–3.75 gm/cc.

Permeability was determined by pumping deionized water at a known rate through a known volume (70 ml loose) of each sample placed in a permeameter designed to stimulate a propped fracture This was done at ambient temperature and at various closure stresses between 500 and 12,000 psi. A constant value of closure stress was maintained by a hydraulic press. The pressure drop across the simulated fracture was recorded as was the propped fracture thickness for each closure stress. The test results ar graphically illustrated in FIG. 1. For additional comparison, the results of permeability testing on 20–40 mesh Ottawa sand is also plotted.

The permeability of the propping agent of the present invention decreases more rapidly with increasing closure stress than does the permeability of the sintered bauxite propping agent. Nevertheless, the propping agent of the present invention maintains a permeability of greater than 100,000 millidarcies at closure pressures of up to 10,000 psi. Even at 12,000 psi, the permeability of the propping agent of the present invention is still very high. These results indicate that the propping agent of the present invention is suitable for high closure stress gas and oil well applications.

Examples 2–4 illustrate that the propping agent of the present invention also meets the American Petroleum Institute's sand specifications for sieve analysis, sphericity and roundness evaluation, and crush resistance. Although Example 5 shows that the acid solubility of the propping agent of the present invention is just outside the American Petroleum Institute sand specifications, the brine exposure test reported in Examples 6 and 7 shows that the propping agent of the present invention has corrosive resistance of the same order as both sintered bauxite and Ottawa sand propping agents. (The American Petroleum Institute has not yet promulgated an official specification for sintered bauxite propping agent.)

EXAMPLE 2

Sieve Analysis

Samples of 100.0 gm of the materials tested in Example 1 were placed in a nest of sieves and shaken for 15 minutes using sieve sizes recommended by American Petroleum Institute procedures. The sample remaining on each sieve was then weighed to determine the percent retained. The results were as follows:

	Percent Retained		
Sieve Size	Propping Agent of Present Invention	Sintered Bauxite	API Specifications (Sand)
16	0.00	0.00	0.00
20	0.00	8.33	≧90.00
30	55.84	60.37	
35	41.28	23.23	
40	2.82	7.66	
50	0.02	0.25	≦1.00
PAN	0.01	0.01	

EXAMPLE 3

Sphericity and Roundness Evaluation

Twenty particles of the materials tested in Example 1 were visually examined for sphericity and roundness using Krumbein's and Sloss' chart for visual estimation of roundness and sphericity. The results were as follows:

Sample	Sphericity	Roundness
Propping Agent of Present Invention	0.9	0.9
Sintered Bauxite	0.9	0.9
API Specification (Sand)	≧0.6	≧0.6

EXAMPLE 4

Crush Resistance

Forty-gram samples of a particular particle size of the materials tested in Example 1 were isolated and placed in a test cell. The cell was placed in a hydraulic press and 12,500 pounds of force was applied for two minutes. The samples where then sieved and the fines collected and weighed. The results were as follows:

Sample	Percent Crushable
Propping Agent of Present Invention	0.20
Sintered Bauxite	0.25
API Specification (Sand)	≦8.00

Samples of the materials tested in Example 1 were dried to a constant weight and 5 gm. were weighed to the nearest 0.1 mg. The sample was treated with 100 ml. of 12% HCl–3% HF in a water bath at 65.6° C/ for 30–35 minutes. The samples were filtered, washed and dried to a constant weight. The weight loss was determined and computed as a percent. The results were as follows:

Sample	Percent Solubility
Propping Agent of Present Invention	2.99
Sintered Bauxite	1.39
API Specification (Sand)	<2.00

(Because of the small sample size, the precision of this test is questionable. For example, other tests with sintered bauxite propping agent have yielded a 7% acid solubility.)

EXAMPLE 6

Brine Exposure

20–40 mesh samples of the materials tested in Example 1 were placed in a test cell and heated to 250° F. For both propping agents, a concentration of 2 lb/ft^2 were used. A liquid brine solution was pumped through the propping agent at a constant rate for a period of 24 hours. The brine solution had the following ingredients: 8% NaCl and 2.5% CaCl. This solution was preheated to match the cell temperature of 250° F. The closure stress on the propping agents were maintained at a constant level of 8,000 psi throughout the test. During the entire test, the pressure drop through the propping agent was recorded in order to determine the permeability decay.

The results of the conductivity decay over time for these two materials is shown in FIG. 2. The conductivities were normalized with respective initial conductivities to enable direct comparison. As can be seen from FIG. 2, the percent decay in the conductivity of the propping agent of the present invention was slightly less than that of the sintered bauxite propping agent.

EXAMPLE 7

Brine Exposure

Tests similar to that of Example 6 were run with 20–40 mesh samples of the propping agent of the present invention tested in Example 1 and Ottawa sand at 4,000 psi. These results are graphically illustrated in FIG. 3. As can be seen from FIG. 3, the percent decay in conductivity is essentially identical for both the propping agent of the present invention and Ottawa sand.

In addition to being useful in hydraulic fracturing of high closure stress (10,000 psi or greater) subterranean formations, the propping agent of the present invention is also useful for medium closure stress (6,000–10,000 psi) applications. Not only will the propping agent of the present invention perform better than sand under such conditions, but also only one third as much propping agent is required. Thus, treatment of medium closure stress subterranean formations with the propping agent or the present invention is an economically feasible alternative to treatment with sand. Examples 8–10 illustrate the comparative effectiveness of the propping agent of the present invention and Ottawa sand at a concentration ratio of 1:3.

EXAMPLE 8

20–40 mesh samples of the propping agent of the present invention tested in Example 1 and Ottawa sand were placed in a test cell and heated to 250° F. at a closure stress of 1,000 psi. Preheated nitrogen at 100 psi was passed through the sample during this period. When the target test temperature was reached, gas flow rates were varied to produce superficial velocities from 1 cm/sec to 30 cm/sec. Gas temperatures at entrance and exit of cell along with cell temperature were recorded. Gas flow rate, sample height and pressure drop along 10 cm. cell length was measured. Each flow was allowed to reach steady state conditions before proceeding to the next flow rate. The above flow ranges were repeated for closure stresses of 2,000, 4,000, 6,000, 8,000 and 10,000 psi. The data was then analyzed producing values at each closure stress for Darcy permeability and conductivity at various flow rates, turbulence factor and absolute permeability. Flow rates were controlled by use of a metering valve placed at the exit of the cell, thus allowing test pressure to be controlled. Flow rates were measured at atmospheric conditions by a thermal flowmeter at high and medium rates and a rotometer for low flow rates. Gas flow rate and density at test conditions was calculated from atmospheric measurements assuming ideal gas behavior and using an average gas temperature pressure in the cell.

Tests were conducted using the propping agent of the present invention at concentrations of 0.5, 1.0 and 1.5 lb/ft^2, and Ottawa sand at concentrations of 1.5, 3.0 and 4.5 lb/ft^2. For the propping agent of the present invention the following results were obtained:

Concentration (lb/ft^2)	Closure Stress (psi)	Turbulence Factor 2 (atm-sec^2/gm)	Conductivity (md/ft)	Permeability (md)	Predicted Beta (atm-sec^2/gm)
0.5	6,000	—	480	—	—
1.0	6,000	2.3×10^{-3}	1,550	139,000	1.3×10^{-3}
1.5	6,000	1.5×10^{-3}	2,270	139,000	1.3×10^{-3}
0.5	8,000	—	210	—	—
1.0	8,000	2.9×10^{-3}	1,030	89,300	2.6×10^{-3}
1.5	8,000	2.0×10^{-3}	1,210	78,000	3.2×10^{-3}
0.5	10,000	—	170	—	—
1.0	10,000	5.7×10^{-3}	520	52,600	6.0×10^{-3}
1.5	10,000	3.1×10^{-3}	750	55,000	5.5×10^{-3}

(Due to the difficulty of measuring sample height at low proppant concentrations, the permeability and turbulence factors for 0.5 lb/ft^2 tests are not reported.)

For Ottawa sand, the following data was obtained:

Concentration (lb/ft^2)	Closure Stress (psi)	Turbulence Factor 2 (atm-sec^2/gm)	Conductivity (md/ft)	Permeability (md)	Predicted Beta (atm-sec^2/gm)
1.5	6,000	—	600	—	—
3.0	6,000	3.1×10^{-3}	1,070	44,000	7.7×10^{-3}
4.5	6,000	3.3×10^{-3}	2,000	106,300	2.0×10^{-3}
1.5	8,000	—	180	—	—
3.0	8,000	2.05×10^{-2}	550	22,520	2.2×10^{-2}
4.5	8,000	7.6×10^{-3}	600	18,500	2.9×10^{-2}
1.5	10,000	—	100	—	—
3.0	10,000	6.91×10^{-2}	200	8,620	9.6×10^{-2}
4.5	10,000	1.0×10^{-2}	280	10,700	6.8×10^{-2}

Because of the effect of turbulance becomes more predominant at increasing velocities, it is not sufficient to compare absolute permeabilities and conductivities alone. Therefore, FIGS. 4 and 5 show Darcy conductivity at two different velocities, which would be encountered in fractured wells producing approximately 1,000 Mscf/D to 10,000 Mscf/D. These figures illustrate that at low flow rates the propping agent of the present invention possesses a conductivity exceeding that of three times the concentration of sand at 6,000 psi and above, and at higher flow rates the propping agent of the present invention has a conductivity exceeding that of three times the concentration of sand at 6,500 psi and above.

EXAMPLE 9

20–40 mesh sample of the propping agent of the present invention tested in Example 1 and Ottawa sand were placed in a test cell in concentrations of 1 lb/ft^2 and 3 lb/ft^2, respectively. The test cell was set up as in Example 8. The closure stress was brought to 4,000 psi and the temperature of the cell increased to 250° F. Preheated nitrogen was flowed through the propping agent as previously described to determine the initial conductivity. Next, a solution of fracturing fluid, broken with an enzyme breaker, was pumped through the propping agent at a low, constant rate for a period of four hours. This simulated the initiation of the clean-up process. The fluid was preheated to approximately 250° F. The same volume of the broken fluid was pumped for each test. This was followed by preheated nitrogen to continue the simulation of the clean-up process. Pressure drop through the sample was monitored until it became a constant. At this time, various flow rates of nitrogen were used to determine the final permeability. The results were as follows:

Propping Agent	Conductivity Initial	(darcy-ft) Final
Propping Agent of Present Invention	1.46	0.20
Ottawa Sand	2.62	0.18

The initial conductivities correspond to measurements made prior to pumping the broken fracturing fluid. The final conductivities were measured after residue damage by the broken fracturing fluid had been accomplished. It is evident from these results that a very large amount of damage occurred in both tests. However, it is interesting to note that even though the conductivity of the propping agent of the present invention was initially much less than the Ottawa sand, the final conductivities were essentially equal. This indicates that less damage was actually incurred on the propping agent of the present invention than on the Ottawa sand.

EXAMPLE 10

Several cases were run on a single phase, two-dimensional, finite difference reservoir simulator. The effects of both formation properties and fracture properties were studied. For each set of formation and fracture properties, two cases were run: one with Ottawa sand as propping agent and another with the propping agent of the present invention tested in Example 1. The propping agent of the present invention was used at a 1:3 ratio (by weight) compared to Ottawa sand. The following properties were held constant for all simulations presented here:

1. New pay thickness 125 ft.
2. Initial closure stress = 8000 psi
3. Initial reservoir pressure = 4000 psi
4. Gas gravity = 0.68
5. Well spacing 640 acres
6. Minimum surface flowing pressure = 1000 psi

The sensitivity to (1) formation permeability, (2) proppant permeability damage by fluid residue, and (3) fracture length are presented in Table 1:

	Cumulative Production Improvement					
	@ 1 year		@ 7 years		@ 15 years	
	MMSCF	%	MMSCF	%	MMSCF	%
Case 1: Formation Perm = 0.008 md, Frac Length = 1600 ft. No Damage Initial Q = 3.5 MMSCF/D	0	0	10	0.2	93	1.6
Case 2: Formation Perm = 0.1 md, Frac Length = 1600 ft. 75% Damage Initial Q = 3.5 MMSCF/D	0	0	533	6.9	925	7.3
Case 3: Formation Perm = 0.1 md, Frac Length = 1100 ft. 50% Damage Initial Q = 3.5 MMSCF/D	0	0	315	3.8	775	5.7
Case 4: Formation Perm = 0.008 md, Frac Length = 1600 ft. No Damage Initial Q = 2 MMSCF/D	0	0	14	0.4	11	0.33

EXAMPLE 11

This Example illustrates a method of making the hydraulic fracturing propping agents of the present invention. It is also recorded as Example 3 of co-pending U.S. Patent application No. 437,321 of Eugene Paul Lunghofer, Sten Mortensen, and Aubrey Ward, filed concurrently herewith on Oct. 28, 1982 for A Process For The Production Of Sintered Bauxite Spheres now U.S. Pat. No. 4,440,866.

The starting material in this example is a bauxitic-kaolin ore from Eufaula, Alabama having the following analysis by weight after ignition at 800° C.: Al_2O_3 50.7%; SiO_2 45.8%; TiO_2 2.60%; Fe_2O_3 0.71%; with the remainder being alkali and alkali-earth metal oxides. An aqueous dispersion of the material as mined is prepared using ball milling or mechanical agitation and addition of 0.25% "DARVAN C" or 0.2% sodium pyrophosphate. Water is added to a solids content of 45%. The pH is adjusted with NaOH to above 8 to insure complete deflocculation and low viscosity. 0.75% "GELVATOL" 20/30 is added as a temporary binder.

This feed, in an amount of 4,000 kg/hour, is passed through pressure nozzles in a fluid bed unit having a fluidizing area of 3 m.2 The velocity of the fluidizing air is 1 2 m/sec, the inlet temperature of the air is 550° C., and the outlet temperature of the air is 70° C. Recycled material introduced through a powder inlet amounts to 1700 kg/hour. The height of the fluidized particle layer is approximately 35 cm. The average residence time of the particles in the fluidized layer is about 15 minutes.

Material is withdrawn in a quantity of 3400 kg/hour, which by sieving is separated into: an oversized fraction having a particle size of about 2.1 mm (50 kg/hour); a course product fraction having a particle size of between 1.2 and 2.1 mm (300 kg/hr); a fine product fraction having a particle size of between 0.6 and 1.2 mm (2450 kg/hour); and an undersized fraction having a particle size below 0.6 mm (600 kg/hour). Also in a bag filter collector unit 300 kg/hour entrained particles are collected and recycled to the tank holding the feed.

The total amount of the oversized fraction together with 400 kg/hour of the fine product fraction is ground in a grinding unit having a sieve of mesh size 3,000 microns, and together with the undersized fraction is lead to the fluid bed unit as seed or nuclei particles. 650 kg/hour of the fine product fraction is recycled without prior grinding.

The remaining material from the product fractions is led through an oven in which the remaining moisture and organic additions (approximately 4% by weight) are removed. The material is then sintered in a rotary kiln at a temperature of approximately 1500° C. for approximately 10 minutes. The sintered particles are then subjected to a further sieving operation to assure that substantially all of the product has the appropriate particle size.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided that they come within the scope of the appended claims and their equivalents.

What is claimed is:

1. A high strength propping agent for use in hydraulic fracturing of subterranean formations comprising solid, spherical particles, said particles having an alumina (A1203) content of between 40 and 60%, a density of less than 3.0 gm/cc and ambient temperature permeability of 100,000 or more millidarcies at 10,000 psi.

2. The propping agent of claim 1 wherein said particles have an alumina (Al_2O_3) content of between 45.5 and 60% and a silica (SiO_2) content of between 36.5 and 51%.

3. The propping agent of claim 1 wherein the composition of said particles comprises: about 50.7% Al_2O_3; about 45.8% SiO_2; about 2.60% TiO_2; and about 0.70% Fe_2O_3; with the remainder being alkali and alkali earth metal oxides

4. The propping agent of claim 1 wherein said particles are made from Eufaula bauxite.

5. The propping agent of claim 4 wherein said Eufaula bauxite includes over 5% gibbsite.

6. The propping agent of claim 4 wherein said Eufaula bauxite has a loss on ignition of between 14.5 and 20%.

7. The propping agent of claim 4 wherein said Eufaula bauxite has a loss on ignition of about 17.1%.

8. The propping agent of claim 1 wherein said particles have a Krumbein sphericity of 0.9 or greater.

9. The propping agent of claim 1 wherein 90% or more of said particles are 30-40 mesh.

10. The propping agent of claim 1 wherein the particles also include a crush strength enhancer selected from the group of nepheline syenite, fused bauxite dust, wollastonite, feldspar and talc.

11. The propping agent of claim 10 wherein the crush strength enhancer is nepheline syenite.

12. The propping agent of claim 1 wherein said particles have been prepared from material comprising naturally occurring ore.

13. The propping agent of claim 12 wherein said naturally occurring ore is Eufaula bauxitic kaolin.

14. The propping agent of claim 12 wherein the density is in the range between 2.62 and 2.80 gm/cc, said particles have been prepared from material comprising naturally occurring ore, and the particles are sintered at a temperature in the range of about 1200° C. to about 1650° C.

15. The propping agent of claim 1 wherein said particles have an alumina content of about 50%.

16. The propping agent of claim 1 wherein said particles have been prepared by sintering.

17. The propping agent of claim 16 wherein said particles have an alumina (Al_2O_3) content of between 45.5 and 60% and a silica (SiO_2) content of between 36.5 and 51%.

18. The propping agent of claim 16 wherein the composition of said particles comprises: about 50.7% Al_2O_3; about 45.8% SiO_2; about 2.60% TiO_2; and about 0.70% Fe_2O_3; with the remainder being alkali and alkali earth metal oxides.

19. The propping agent of claim 16 wherein said particles are made from naturally occurring ore, and the sintering is at temperatures in the range of about 1200° to about 1650° C.

20. The propping agent of claim 19 wherein the naturally occurring ore is Eufaula bauxitic kaolin.

21. The propping agent of claim 20 wherein said Eufaula Bauxite includes over 5% gibbsite.

22. The propping agent of claim 20 wherein said Eufaula Bauxite has a loss on ignition of between 14.5 and 20%.

23. The propping agent of claim 1 wherein said particles have a Krumbein sphericity of 0.9 or greater, 90% or more of said particles are 30-40 mesh, and the particles also include a crush strength enhancer selected from the group of nepheline syenite, fused bauxite dust, wollastonite, feldspar and talc.

24. The propping agent of claim 1 wherein said particles have a density between 2.62 and 2.80 gm/cc, and said particles have been prepared from naturally occurring ore by sintering at temperatures in the range of about 1200° C. to about 1650° C.

25. The propping agent of claim 24 wherein said particles have an alumina (Al_2O_3) content of between 45.5 and 60% and a silica (SiO_2) content of between 36.5 and 51%.

26. The propping agent of claim 25 wherein the composition of said particles comprises: about 50.7% Al_2O_3; about 45.8% SiO_2; about 2.60% TiO_2; and about 0.70% Fe_2O_3; with the remainder being alkali and alkali earth metal oxides.

27. The propping agent of claim 24 wherein said particles are made from Eufaula bauxitic kaolin.

28. The propping agent of claim 27 wherein said bauxitic kaolin includes over 5% gibbsite, said particles have a Krumbein sphericity of 0.9 or greater, 90% or more of said particles are 30-40 mesh, and the particles also include a crush strength enhancer selected from the group of nepheline syenite, fused bauxite dust, wollastonite, feldspar and talc.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,120,455
DATED : June 9, 1992
INVENTOR(S) : Eugene P. Lunghofer

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

At column 4, line 66, change "Krum being" to --Krumbein--.

At column 6, lines 60-61, insert --EXAMPLE 5--
--Acid Solubility--.

At column 7, line 55, change "agent or the present" to --agent of the present--.

At column 8, line 28, change "Factor2" to --Factor--.

At column 8, line 47, change "Factor2" to --Factor--.

At column 11, line 5, change "area of 3 m.2 The" to --area of 3 m.^{2}. The--.

At column 11, line 6, change "is 1 2 m/sec" to --is 1.2 m/sec--.

At column 11, line 49, change "mina (A1203) content" to --mina (Al_2O_3) content--.

Signed and Sealed this

Twenty-fifth Day of January, 1994

Attest:

Bruce Lehman

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

[redacted]

EXHIBIT 6

United States Patent [19]
Fitzgibbon

[11] **Patent Number:** **4,879,181**
[45] **Date of Patent:** **Nov. 7, 1989**

[54] SINTERED SPHERICAL PELLETS CONTAINING CLAY AS A MAJOR COMPONENT USEFUL FOR GAS AND OIL WELL PROPPANTS

[75] Inventor: **Jeremiah J. Fitzgibbon**, Lafayette, La.

[73] Assignee: **Carbo Ceramics Inc., Irving, Tex.**

[21] Appl. No.: **40,534**

[22] Filed: **Apr. 20, 1987**

Related U.S. Application Data

[60] Continuation of Ser. No. 712,909, Mar. 15, 1985, abandoned, and a continuation-in-part of Ser. No. 347,210, Feb. 9, 1982, abandoned, which is a continuation of Ser. No. 565,429, Dec. 27, 1983, abandoned, wbich is a division of Ser. No. 405,055, Aug. 4, 1982, Pat. No. 4,427,068, which is a continuation-in-part of Ser. No. 347,210, Feb. 9, 1982, abandoned.

[51] **Int. Cl.^{4}** **B32B 18/00**; C09K 7/00
[52] **U.S. Cl.** **428/402**; 252/8.551; 428/403; 501/127; 501/128
[58] **Field of Search** .... 428/402, 403; 501/127, 501/128; 252/855 R

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Primary Examiner—George F. Lesmes
Assistant Examiner—J. Davis
Attorney, Agent, or Firm—Pravell, Gambrell, Hewitt, Kimball & Krieger

[57] ABSTRACT

Sintered, spherical composite pellets or particles comprising one or more clays as a major component and bauxite, alumina, or mixtures thereof, are described, along with the process for their manufacture. The pellets may have an alumina-silica (Al_2O_3—SiO_2) ratio from about 9:1 to about 1:1 by weight. The use of such pellets in hydraulic fracturing of subterranean formations is also described.

14 Claims, No Drawings

SINTERED SPHERICAL PELLETS CONTAINING CLAY AS A MAJOR COMPONENT USEFUL FOR GAS AND OIL WELL PROPPANTS

This is a continuation of application Ser. No. 712,909 filed Mar. 15, 1985, now abandoned, which is a file wrapper continuation application of application Ser. No. 565,429, filed Dec. 27, 1983, abandoned which is a division of application Ser. No. 405,055, filed Aug. 4, 1982, now U.S. Pat. 4,427,068, which is a continuation-in-part of application Ser. No. 347,210, filed Feb. 9, 1982, abandoned, which is a continuation-in-part of application Ser. No. 347,210, filed Feb. 9, 1982 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to oil and gas well proppants and, more particularly, to sintered proppants containing clay as a major component, a method of making such proppants, and to a method of maintaining a fracture in a subterranean formation in a propped condition by utilizing such proppants.

2. History of the Prior Art

Oil and natural gas are produced from wells having porous and permeable subterranean formations. The porosity of the formation permits the formation to store oil and gas, and the permeability of the formation permits the oil or gas fluid to move through the formation. Permeability of the formation is essential to permit oil and gas to flow to a location where it can be pumped from the well. Sometimes the permeability of the formation holding the gas or oil is insufficient for economic recovery of oil and gas. In other cases, during operation of the well, the permeability of the formation drops to the extent that further recovery becomes uneconomical. In such cases, it is necessary to fracture the formation and prop the fracture in an open condition by means of a proppant material or propping agent. Such fracturing is usually accomplished by hydraulic pressure, and the proppant material or propping agent is a particulate material, such as sand, glass beads or ceramic particles, which are carried into the fracture by means of a fluid.

Spherical particles of uniform size are generally acknowledged to be the most effective proppants due to maxiized permeability. For this reason, assuming other properties to be equal, spherical or essentially spherical proppants, such as rounded sand grains, metallic shot, glass beads and tabular alumina, are preferred.

In practice, in deep wells, where high pressures are encountered, e.g., above about 700 Kg/cm^2 (10,000 psi), the foregoing specifically mentioned proppants are either entirely ineffective or do not exhibit desired permeability. Examples of prior art proppants and their use are found in U.S. Pat. Nos. 2,950,247, McGuire et al; 3,026,938, Huitt et al; 3,126,056, Harrell; 3,497,008, Graham et al; 3,976,138, Colpoys et al; and 4,068,718, Cooke et al. One of the better proppants useful at high pressures, disclosed in U.S. Pat. No. 3,976,138, is alumina. However, even alumina, as disclosed in U.S. Pat. No. 3,976,138, has reduced permeability at pressures in excess of 350 Kg/cm^2 (5,000 psi).

As disclosed in U.S. Pat. No. 4,068,718, sintered bauxite unexpectedly has a permeability which is superior to the previously mentioned proppant materials at pressures as high as 700 Kg/cm^2 (10,000 psi) or higher.

Unfortunately, the sintered bauxite material actually used in making the measurements disclosed in U.S. Pat. No. 4,068,718 does not have a desired spherical shape, which would provide high permeability.

The prior art sintered bauxite particles may be produced in spherical shape as described in R. J. Seider's commonly assigned, copending U.S. patent application Ser. No. 252,491, filed Apr. 8, 1981, as a continuation of U.S. patent application Ser. No. 969,122, filed Dec. 13, 1978. However, such proppants, although extremely useful under high pressure conditions, over about 700 Kg/cm^2 (10,000 psi), are costly. The cost of the prior art sintered bauxite proppant for wells of intermediate pressures, between about 350 and 700 Kg/cm^2 (5,000 and about 10,000 psi), may not be economically justified. The present invention provides proppants aptly suited to use under pressures of up to about 700 Kg/cm^2 (10,000 psi), which are more economical and have lower specific gravities and bulk densities, which would benefit the user, in that fewer pounds of proppant per cubic foot of fracture would be required. Handling, e.g., pumping of slurries of lower density material, is also made easier.

BRIEF DESCRIPTION OF THE INVENTION

In accord with the present invention, composite, spherical pellets or particles containing clay as a major component, having an alumina to silica dry weight basis ratio from about 9:1 to about 1:1 and apparent specific gravities less than 3.40, are produced. Diaspore clay, burley clay and flint clay have been found to be useful in the manufacture of such pellets although it is believed that other clays may be employed. Such spherical particles are useful as oil and gas well proppants.

The present calcined clay materials are particularly adapted to use in combination with known, prior art proppant materials, for example, bauxite or alumina, to produce composite sinterable, spherical pellets which are subsequently furnaced to produce sintered, spherical pellets eminently useful as proppants. The composites of the present invention contain a major portion and, more preferably, greater than about 40 percent by weight, of clay. Diaspore clay is preferred and combinations containing up to 95 percent by weight diaspore clay are useful.

The clay materials of the present invention are compatible with, and may be used as a matrix for, a wide variety of proppant materials, and, in this manner, a wide variety of composite proppants may be produced, which may be customized to particular conditions or formations. Thus, the properties of the final sintered composite pellets, such as strength, permeability, specific gravity, bulk density and acid resistance, may be controlled through variations in the initial component mixture.

Combinations of diaspore clay and bauxite are particularly useful. Such mixtures may suitably contain up to 95 percent by weight clay. Mixtures containing up to 80 percent by weight clay have a broad range of use, and mixtures containing 50 to 60 percent by weight clay have a particularly broad range of use.

The present invention also provides a process for propping fractures in oil and gas wells at depths of 7,000 to 14,000 feet utilizing the present sintered pellets by mixing the pellets with a fluid, such as oil or water, and introducing the mixture into a fracture in a subterranean formation. The compaction pressure upon the fracture generally is at least 280 Kg/cm^2 (4,000 psi) and usually is in the range of from about 350 to about 700 Kg/cm^2 (5,000 to about 10,000 psi). The present pellets have an average particle size between 0.1 and 2.5 millimeters. It has been found that the present composite pellets containing 50 percent or more parts by weight clay, at pressures up to about 700 Kg/cm^2 (10,000 psi), have desirable permeability characteristics, i.e., they exhibit a permeability to brine at about 93.3° C. (200° F.) which decreases not more than about three-fourths when the pressure applied to them is increased from 140 to 700 Kg/cm^2 (2,000 to 10,000 psi).

The present proppant materials are produced by forming a mixture comprised of clay with a material, such as bauxite or alumina. The starting ingredients have an average particle size of less than about 15 microns and, preferably, less than about 10 microns and, most preferably, less than about 5 microns.

In a preferred method, the mixture is produced on an intensive mixer having a rotatable table provided with a rotatable impacting impeller, such as described in U.S. Pat. No. 3,690,622, to Brunner. Sufficient water is added to cause essentially spherical ceramic pellets to form, and, after such pellets have formed, from about 5 to about 15 percent of additional ceramic powder by weight of pellets is added, and the mixer is further operated to cause accretion of the added material to the pellets being formed.

The resulting pellets are then dried at between about 100 and about 300 degrees centigrade and furnaced at sintering temperature until an apparent specific gravity between about 2.70 and about 3.40 is obtained, depending on the composition of the starting mixture.

DETAILED DESCRIPTION OF THE INVENTION

The sintered composite proppant pellets of the present invention have apparent specific gravities less than 3.40 and are spherical in shape.

The sphericity of the pellets may be determined using a visual comparator. Krumbein and Sloss, Stratigraphy and Sedimentation, second edition, 1955, W.H. Freeman & Co., San Francisco, Calif., describe a chart for use in visual determination of sphericity and roundness. Visual comparison using this chart is a widely used method of evaluating sphericity or roundness of particles. In using the visual comparison method, a random sample of 10 to 20 particles of the material to be tested is selected. The particles are viewed under a 10 to 20 power microscope or a photomicrograph and their shapes compared to the Krumbein and Sloss chart. The chart values for sphericity range from 0.3 to 0.9. The chart values for the individual particles are then averaged to obtain a sphericity value. The present particles have an average sphericity of about 0.8 or greater when visually compared with the Krumbein and Sloss chart.

"Spherical" and related forms, as used herein, is intended to mean an average ratio of minimum diameter to maximum diameter of about 0.80 or greater, or having an average sphericity value of about 0.8 or greater compared to a Krumbein and Sloss chart.

"Bulk density", as used herein, is the weight per unit volume, including in the volume considered, the void spaces between the particles.

"Apparent specific gravity" is a number without units, but numerically equal to the weight in grams per cubic centimeter of volume, excluding void space or open porosity in determining the volume. The apparent specific gravity values given herein were determined by liquid (ethylbenzene) displacement.

"Theoretical density" and "true specific gravity" exclude not only the void space between particles and open porosity of particles from the volume, but also exclude closed porosity. These latter two measures are not customarily used for characterizing proppants. Theoretical density and true specific gravity require fine grinding to expose any closed porosity.

Unless otherwise stated at the point of interest, all percentages, proportions and values with respect to composition are expressed in terms of weight.

The sintered, spherical pellets of the present invention may be manufactured by furnacing a composite clay mixture. Various sintering aids may be incorporated with the starting mixture, for example, minor amounts of bentonite clay or iron oxide, boron, boron carbide, aluminum diboride, boron nitride, boron phosphide and other boron compounds. If sintering aids are used, generally up to about 30 weight percent are found useful. The most desirable range of sintering aid can be readily determined by those skilled in the art, depending upon the particular clay mixture used. Fluxes, such as sodium carbonate, lithium carbonate, feldspar, manganese oxide, titania, iron oxide and sodium silicates, up to about 30 weight percent, may be added to aid sintering. If desired, a binder, for example, various resins or waxes known in the prior art, may be added to the initial mixture to improve pelletizing and to increase the green strength of the unsintered pellets.

Pellets according to the present invention and for use with the present invention may be prepared from a mixture of any of the clays described in Table I with bauxite or alumina or mixtures of these. The composition of the specific bauxite employed in the manufacture of the pellets described herein is also given in Table I. All values in Table I are expressed as percentages by weight. Where an omission occurs, it indicates that sufficient testing was not conducted to obtain a value.

TABLE I

(Typical Analysis of Bauxite and Clays - calcined)

Chemical Compound	Surinam Bauxite	High Purity Diaspore Clay	High Silica Diaspore Clay	High Iron (Brown) Diaspore Clay	Burley Clay	Flint Clay
Al_2O_3	86.80	75.10	70.00	78.30	54.07	38.52
SiO_2	3.42	18.60	24.40	15.09	41.33	56.64
Fe_2O_3	4.74	0.80	.80	2.63	1.26	0.65
TiO_2	3.13	2.99	3.04	3.05	2.45	3.49
Other (e.g. MgO, CaO)	1.00	1.51	—	0.72	0.74	0.67
Loss on Ignition	0.91	1.00	—	0.21	0.15	0.03

TABLE I-continued

(Typical Analysis of Bauxite and Clays - calcined)

Chemical Compound	Surinam Bauxite	High Purity Diaspore Clay	High Silica Diaspore Clay	High Iron (Brown) Diaspore Clay	Burley Clay	Flint Clay
Apparent Specific Gravity After Calcining g/cc	3.6-3.7	2.9-3.1	2.9-3	2.9-3.1	2.7-2.8	2.5-2.6

Each of the clays described in Table I may be obtained from Missouri Minerals Processing, High Hill, Mo. 63350, in calcined form.

The Surinam bauxite described in Table I may be obtained from Aluminum Company of America, Pittsburgh, Pa. 15219. Surinam bauxite is so designated for that is the country in which it is mined. It is expected that other bauxites may be substituted without departing from the present invention.

Disaspore clays, as found in nature, are predominantly hydrated aluminum oxide ($Al_2O_3.H_2O$). Such clays occur in emery rock in association with corundum. The main deposits of diaspore clays in the United States are in Missouri and Pennsylvania. Diaspore clays have a hardness between 6.5 and 7.0 and a true specific gravity usually between 3.30 and 3.45 gm/cm3. The crystal structure of diaspore clay is orthorhombic. Typically, diaspore clay, as found in nature, contains 25 to 30 percent by weight, and, in some cases, as high as 35 percent by weight, of impurities. Generally, the major impurities are: SiO_2, which typically ranges from about 12 to about 25 percent by weight; TiO_2, which typically ranges from about 2.75 to 3.75 percent; Fe_2O_3, typically between 0.25 and 1.0 percent; and MgO and CaO, generally less than 1.0 percent.

The clay materials for use in the present invention are initially calcined, by known prior art methods, at temperatures and times sufficiently high to remove any organic material and to substantially remove water of hydration.

The sintered, spherical pellets of the present invention are preferably made as follows:

1. Starting ingredients of calcined clay and alumina, bauxite, or mixtures thereof, are added in a predetermined ratio to a high intensity mixer. At least 40 percent of the total ingredients on a dry weight basis is clay. Each of the ceramic ingredients has an average particle size of less than about 15 microns and preferably less than about 10 microns and most preferably, less than about 5 microns.

The small particle size is required in order to obtain a finished spherical sintered pellet having the desired density. An average particle size of smaller than 5 microns is desirable, and the average particle size is most preferably below 3 microns and usually above 0.5 microns.

2. The powdered ceramic starting ingredients are stirred to form a dry homogeneous particulate mixture having an average particle size of less than about 15 microns.

A preferred stirring or mixing device is that obtainable from Eirich Machines, Inc., known as the Eirich Mixer. A mixer of this type is provided with a horizontal or inclined circular table, which can be made to rotate at a speed of from about 10 to about 60 revolutions per minute (rpm), and is provided with a rotatable impacting impeller, which can be made to rotate at a tip speed of from about 5 to about 50 meters per second. The direction of rotation of the table is opposite that of the impeller, causing material added to the mixer to flow over itself in countercurrent manner. The central axis of the impacting impeller is generally located within the mixer at a position off center from the central axis of the rotatable table. The table may be in a horizontal or inclined position, wherein the incline, if any, is between 0 and 35 degrees from the horizontal.

3. While the mixture is being stirred, there is added sufficient water to cause formation of composite, spherical pellets from the ceramic powder mixture.

In general, the total quantity of water which is sufficient to cause essentially spherical pellets to form is from about 17 to about 20 percent by weight of the initial starting ceramic ingredients and usually between about 18 and about 20 percent by weight of the initial ceramic powder. The total mixing time usually is from about 2 to about 6 minutes.

After the clay mixture is added to the mixer, the table is rotated at from about 10 to about 60 rpm and, preferably, from about 20 to about 40 rpm, and the impacting impeller is rotated to obtain a tip speed of from about 25 to about 50, preferably, from about 25 to about 35, meters per second, and sufficient water is added to cause essentially spherical pellets of the desired size to form. If desired, the impeller may be initially rotated at from about 5 to about 20 meters per second during addition of one-half of the sufficient water and subsequently rotated at the higher tip speed of 25 to about 50 meters per second during the addition of the balance of the water. The rate of water addition is not critical. The intense mixing action quickly disperses the water throughout the particles.

4. The resulting pellets are dried at a temperature of between about 100° (212° F.) and about 300° C. (572° F.) until preferably less than 3 percent and, most preferably, less than 1 percent moisture remains in the pellets. The most preferred drying temperature is between about 175° (347° F.) and 275° C. (527° F.), and the drying time is usually between about 30 and about 60 minutes.

5. The dried pellets are then furnaced at sintering temperature for a period sufficient to enable recovery of sintered, spherical pellets having an apparent specific gravity of between 2.70 and 3.40 and a bulk density of from about 1.35 to about 1.80 grams per cubic centimeter. The specific time and temperature to be employed is, of course, dependent on the starting ingredients and is determined empirically according to the results of physical testing of pellets after furnacing. The furnacing step is carried out to sinter the composite pellets; gener-

ally, temperatures of between about 1,350° C. (2,462° F.) and about 1,550° C. (2,822° F.) for about 4 to about 20 minutes and, more preferably, from about 1,485° (2,705° F.) to about 1,515° C. (2,759° F.) for about 4 to about 8 minutes, are useful, depending upon the sintering aids and fluxes which may be included.

While the process just described hereinabove will yield pellets according to the invention, it is preferred that from about 5 to about 15 percent and, preferably, from about 8 to about 10 percent of additional starting ingredients by weight of pellets be added, after the addition of water but prior to drying of the pellets. The added material is of the same composition as that described in step 1. The addition of more dry ceramic powder is followed by rotating the impeller at a tip speed of between about 5 and about 20 meters per second, preferably, between about 10 and about 20 meters per second, for from about 1 to about 6 minutes, while continuing to rotate the table at from about 10 to about 60 rpm and, preferably, from about 20 to about 40 rpm. This step improves yield and results in improved sphericity of the pellets.

If desired, the rotation of the impeller may then be stopped while the table continues to rotate for between about 1 and about 5 minutes.

The impacting impeller is preferably a disk provided with peripheral rods or bars attached to the disk. The longitudinal axis of the rods or bars is desirably essentially parallel with the axis of rotation of the impeller, which is usually a vertical axis. The diameter of the impeller is measured from the axis of rotation to the center of the most distant rod or bar. Tip speed is the speed of the most distant rod or bar.

The diameter of the impeller depends upon the size of the mixer but is usually less than 25 percent of the diameter of the mixer. The impeller in most applications is between 10 and 100 centimeters in diameter and usually rotates at from 200 to 3,750 rpm at the lower tip speeds of 10 to 20 meters per second, depending upon impeller diameter, and at from 500 to 6,500 rpm at the higher tip speeds of 25 to 35 meters per second, depending upon impeller diameter.

The pellets are screened for size preferably after drying. However, they may be screened before drying or after furnacing. The rejected oversized and undersized pellets and powdered material obtained after the drying and screening steps may be recycled. The finished pellets may be tumbled to enhance smoothness. The resultant sintered pellets have a bulk density ranging from about 1.35 to about 1.85 grams per cubic centimeter, depending upon the ceramic starting ingredients employed.

The overall particle size of the pellets for use as propping agent for increasing permeability in a subterranean formation penetrated by well is between 0.1 and about 2.5 millimeters and preferably between about 0.15 and 1.7 millimeters.

In Table II is summarized the composition for several pellets according to the invention produced from the raw material indicated. Also given are the results of testing of these pellets. Unless otherwise indicated, parts and percentages are by weight. All samples were prepared in accord with the procedures given herein. Example 1 gives in detail the procedure employed in the preparation of Sample No. 2, which procedure is typical of that employed in preparation of the remainder of the samples reported in Table II.

TABLE II

			SAMPLE NO.				
INGREDIENTS			1 50% DIASPORE CLAY 50% SURINAM BAUXITE	2 60% DIASPORE CLAY 40% BAUXITE	70% DIASPORE CLAY 30% BAUXITE	4 80% DIASPORE CLAY 20% BAUXITE	5 90% DIASPORE CLAY 10% BAUXITE
Composition of furnaced pellets							
Al_2O_3			82.10	79.78	78.61	77.44	76.27
SiO_2			9.31	12.52	14.04	15.56	17.08
Al_2O_3—SiO_2 ratio (based on % by wgt.)			8.82	6.37	5.60	4.98	4.46
Fe_2O_3			3.14	2.36	1.97	1.58	1.19
TiO_2			3.06	3.04	2.88	3.02	3.01
Other			2.39	2.30	2.50	2.40	2.45
Roundness			—	.86	—	.78	—
Sphericity			—	.85	—	.75	—
Acid Solubility (12% Hydrochloric, 3% Hydrofluoric)			—	5.42	4.86	5.73	—
Bulk Density							
grams/cubic centimeter			—	1.79	1.70	1.63	1.53
pounds/cubic foot			—	112	106	102	96
Apparent Specific Gravity grams/cubic centimeter			—	3.27	3.20	3.10	3.07
API Crush (% fines)							
7500 psi			—	—	—	7.24	—
10000 psi			—	9.9	5.88	11.61	12.27
	Applied Pressure psi	Applied Pressure Kg/cm^2					
Permeability, Darcies at .125" fracture width	2000	140	—	225	195	156	162
	4000	281	—	193	180	139	134
	6000	422	—	163	151	113	108
	8000	562	—	138	122	85	84
	10000	703	—	113	95	69	61

TABLE II-continued

	12000	844	—	88	73	44	41
	14000	984		64	55	32	21
% decrease in permeability 2000–10,000 psi			—	50	51	56	62

INGREDIENTS			SAMPLE NO. 6 95% DIASPORE CLAY 05% BAUXITE	7 70% BURLEY CLAY 30% BAUXITE	8 50% FLINT CLAY 50% BAUXITE	9 65% FLINT CLAY 35% BAUXITE	10 75% FLINT CLAY 25% BAUXITE
Composition of furnaced pellets							
Al_2O_3			75.68	63.91	62.65	55.41	50.58
SiO_2			17.84	29.93	30.00	37.98	43.30
Al_2O_3—SiO_2 ratio (based on % by wgt.)			4.24	2.14	2.09	1.46	1.17
Fe_2O_3			1.00	2.32	2.70	2.11	1.71
TiO_2			3.01	2.68	3.30	3.37	3.41
Other			17.53	1.16	1.35	1.13	1.00
Roundness			.80	.84	.81	.81	.84
Sphericity			.82	.82	.82	.80	.81
Acid Solubility (12% Hydrochloric, 3% Hydrofluoric)			6.28	7.40	4.96	4.83	4.60
Bulk Density							
grams/cubic centimeter			1.51	1.47	1.53	1.43	1.40
pounds/cubic foot			95	92	95.5	89	88
Apparent Specific Gravity grams/cubic centimeter			3.05	2.86	2.83	2.79	2.75
API Crush (% fines)							
7500 psi			—	—	—	3.55	8.51
10000 psi			—	17.48	11.30	—	—
	Applied Pressure psi	Kg/cm²					
Permeability, Darcies at .125" fracture width	2000	140	109	198	250	185	225
	4000	281	98	180	222	172	210
	6000	422	84	137	169	134	173
	8000	562	65	91	116	90	112
	10000	703	37	56	74	55	64
	12000	844	20	32	46	32	35
	14000	984	11	18	27	16	17
% decrease in permeability 2000–10,000 psi			66	72	70	70	72

— = not tested

The test procedures and apparatus employed to test the permeability in darcies of the pellets of the present invention included placing a predetermined quantity of the material to be tested between two parallel hardened steel plates, applying force tending to close the initially established 0.125 inch gap between the plates, then measuring the flow rate through the packed cell using brine (2 percent KCl) at 93.3° C. (200° F.) at various applied stresses or pressures. The particle size distribution of the pellets was 20×40 mesh, U.S. Standard Sieves (ninety percent by weight minimum of pellets will pass through 20 mesh [841 micron] screen but not through 40 mesh [420 micron] screen).

Values obtained using the American Petroleum Institute (API) procedure for determining resistance to crushing are also reported in Table II. According to this procedure, a bed of about 6 mm depth of sample to be tested is placed in a hollow cylindrical cell. A piston is inserted in the cell. Thereafter, a load is applied to the sample via the piston. One minute is taken to reach maximum load which is then held for two minutes. The load is thereafter removed, the sample removed from the cell, and screened to separate crushed material. The results are reported as a percentage by weight of the original sample.

Acid solubility of the samples reported in Table II was tested in accordance with recommended API test procedure, fourth draft, June 1980. In this procedure a known weight of sample (5 g) is placed in a 150 ml polyethylene beaker containing 100 ml of 12%-3% HCl-HF acid. The sample acid containing beaker is then placed in a 65.6° C. (150° F.) water bath for 30 to 35 minutes. The sample is not stirred. The sample is thereafter filtered through a previously weighed filter crucible or funnel and washed three times with 20 ml portions of distilled water. The filtered and washed sample is thereafter dried to constant weight (approximately one hour) at 105° C. (220° F.). The values given in Table II represent the percentage of weight lost or dissolved due to the acid.

Sphericity of the pellets reported in Table II was determined using a Krumbein and Sloss chart. The values reported represent an average of 10-20 pellets per sample.

Roundness as reported in Table II is a measure of the relative sharpness of the pellet corners, or of curvature. This evaluation may be done at the same time and on the same sample as that used for sphericity. The pellets are visually compared with a Krumbein and Sloss chart. The values reported represent an average of 10–20 pellets per sample.

Bulk density values reported in Table II were determined by weighing that amount of sample that would fill a cup of known volume.

EXAMPLE 1

About 81 kilograms of diaspore clay material that had been previously calcined at a temperature sufficiently high to remove any organic materials and substantially all of the water of hydration from the clay, together with about 54 kilograms of bauxite (60% by weight clay) powder having an average particle size of between 4 and 8 microns were added to an Eirich mixer having a table diameter of about 115 centimeters, an operating capacity of about 160 kilograms and an impacting impeller diameter of about 27 centimeters.

The table was rotated at about 35 rpm, and the impeller was rotated at about 1,090 rpm, and about 27 kilograms of water was added. Rotation of the table and impeller was continued for about 1 minute; subsequently, the impeller speed was increased to about 2,175 rpm. The table and impeller were rotated until seed pellets were formed, less than 5 percent of which were of a size smaller than 0.50 mm (about 3 minutes). The impeller was then reduced to about 1,090 rpm, and about 4.08 kilograms of the initial diaspore clay - bauxite powder mixture was added. Rotation of the pan and impeller was then continued for an additional 2 minutes to form spherical pellets.

The pellets were then dried for about 20 minutes at about 110° C. (230° F.) in a rotary dryer and then fired at about 1,500° C. (2,732° F.) for about 5 minutes. The yield of useful pellets having a size between 150 and 1,700 microns (0.15 and 1.7 millimeters) was greater than 90 percent by weight of starting ceramic powder. The resulting pellets had an apparent specific gravity of about 3.25, a bulk density of 1.79 gm/cm$_3$ and a sphericity of greater than 0.8, as determined using the Krumbein and Sloss chart.

The permeability in darcies of the pellets like Sample 2 was determined in 2% KCl solution at 93.3° C. (200° F.) at various applied pressures. The results are shown in Table III.

TABLE III

60% Diaspore Clay/40% Bauxite		
Applied Pressure		
(Kg/cm^3)	(psi)	Permeability (Darcies)
122.5	1742	233
245.0	3485	199
367.5	5227	176
490.0	6969	150
612.5	8712	128
735.0	10454	102

The crush strength of the pellets like Sample 2 was tested by measuring the compressibility of the pellets by placing a bed of about 6 millimeters of furnaced pellets in a cylinder and applying pressure by means of a piston. The amount of pressure required to induce various fixed amounts of compaction was measured. The results are shown in Table IV.

TABLE IV

60% Diaspore Clay/40% Bauxite		
	Pressure Required	
Compaction Induced	Kg/cm^2	psi
0.254 mm (0.010 inch)	119	1693
0.508 mm (0.020 inch)	238	3385
0.762 mm (0.030 inch)	399	5675
1.016 mm (0.040 inch)	581	8264
1.270 mm (0.050 inch)	749	10,653
1,524 mm (0.060 inch)	959	13,640
1.778 mm (0.070 inch)	1,155	16,428

The composite, spherical, sintered pellets of the present invention are useful as a propping agent in methods of fracturing subterranean formations to increase the permeability thereof, particularly those formations having a compaction pressure of at least 280 Kg/cm^2 (4000 psi), which are typically located at a depth 6,000 feet or greater. Pellets according to the present invention are presently believed to be particularly suitable for use at depths greater than 7,000 feet but less than 14,000 feet.

When used as a propping agent, the pellets of the present invention may be handled in the same manner as other propping agents. The pellets may be delivered to the well site in bags or in bulk form along with the other materials used in fracturing treatment. Conventional equipment and techniques may be used to place the spherical pellets as propping agent.

A viscous fluid, frequently referred to as "pad", is injected into the well at a rate and pressure to initiate and propagate a fracture in the subterranean formation. The fracturing fluid may be an oil base, water base, acid, emulsion, foam, or any other fluid. Injection of the fracturing fluid is continued until a fracture of sufficient geometry is obtained to permit placement of the propping pellets. Thereafter, pellets as hereinbefore described are placed in the fracture by injecting into the fracture a fluid into which the pellets have previously been introduced and suspended. The propping distribution is usually, but not necessarily, a multi-layer pack. The overall particle size of the pellets is between about 0.1 and about 2.5 millimeters and, more preferably, between about 0.15 and about 1.7 millimeters. Following placement of the pellets, the well is shut-in for a time sufficient to permit the pressure in the fracture to bleed off into the formation. This causes the fracture to close and apply pressure on the propping pellets which resist further closure of the fracture.

The foregoing description and embodiments are intended to illustrate the invention without limiting it thereby. It will be understood that various modifications can be made in the invention without departing from the spirit or scope thereof.

I claim:

1. A gas and oil well proppant comprising a plurality of composite, sintered, spherical pellets having a permeability to brine at about 200° F. (93.3° C.) which deceases not more than about three-fourths when the applied pressure on said pellets is increased from 2,000 to 10,000 psi (140 to 700 kg/cm^2), said pellets being prepared from a mixture of calcined clay and calcined bauxite, said mixture containing at least 40 percent clay on a dry weight basis, and said pellets having an alumina to silica ratio on a dry weight basis from about 9:1 to 1.17:1, more than 6.12 weight percent of other than alumina and silica, a diameter of between 0.1 and about 2.5 millimeters, an apparent specific gravity of less than

3.40 but greater than 2.75 g/cc and a bulk density greater than 88 lbs./cubic ft.

2. The proppant of claim 1, wherein the pellets have an alumina to silica dry weight basis ratio from about 4:1 to about 6.5:1.

3. The proppant of claim 2, wherein the pellets have an alumina to silica ratio of about 5:1.

4. The proppant of claim 1, wherein said pellets have an apparent specific gravity from about 3.0 to about 3.3 and an alumina to silica ratio on a dry weight basis from about 4:1 to about 6.5:1.

5. The proppant of claim 1, wherein said pellets have at least 90 percent by weight of Al_2O_3 and SiO_2.

6. The proppant of claim 5, wherein the clay is diaspore, flint or burley.

7. The proppant of claim 1, wherein the pellets have not more than about 82 percent by weight of Al_2O_3.

8. The proppant of claim 1, wherein the pellets are prepared from at least 40 percent by weight of diaspore clay.

9. The proppant of claim 8, wherein said pellets are prepared from at least 60 percent by weight of diaspore clay.

10. The proppant of claim 1, wherein the pellets are prepared from disapore clay and bauxite.

11. The proppant of claim 10 wherein the pellets are prepared from at least 60 percent by weight of disapore clay.

12. The proppant of claim 1, wherein the pellets are prepared from about 80 percent by weight of disapore clay and about 20 percent by weight of Surinam bauxite.

13. The proppant of claim 1, wherein the pellets are prepared from about 70 percent by weight of burley clay and about 30 percent by weight of bauxite, said pellets having an apparent specific gravity of about 2.86.

14. The proppant of claim 1, wherein the pellets are prepared from about 50 to about 75 percent by weight of flint clay and from about 50 to about 25 percent by weight of bauxite.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 4,879,181
DATED : November 7, 1989
INVENTOR(S) : Jeremiah J. Fitzgibbon

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

At column 1, lines 11-13 delete "which is a continuation-in-part of application Ser. No. 347,210, filed Feb. 9, 1982, abandoned,".

At column 1, line 48, change "maxiized" to --maximized--.

At column 5, line 24, change "$(Al_2O_3.H_2O)$" to --$(Al_2O_3 \cdot H_2O)$--.

At column 5, line 29, change "gm/cm$_3$" to --gm/cm^3--.

At column 8, top of third column in Table II, insert --3--.

At column 11, line 42, change "gm/cm$_3$" to --gm/cm^3--.

At column 12, line 58, change "deceases" to --decreases--.

Signed and Sealed this

Twenty-first Day of April, 1992

Attest:

HARRY F. MANBECK, JR.

Attesting Officer

Commissioner of Patents and Trademarks

US004879181B1

REEXAMINATION CERTIFICATE (2184th)

United States Patent [19]

[11] **B1 4,879,181**

Fitzgibbon

[45] Certificate Issued **Jan. 11, 1994**

[54] **SINTERED SPHERICAL PELLETS CONTAINING CLAY AS A MAJOR COMPONENT USEFUL FOR GAS AND OIL WELL PROPPANTS**

[75] Inventor: **Jeremiah J. Fitzgibbon**, Lafayette, La.

[73] Assignee: **Carbo Ceramics Inc.**, Irving, Tex.

Reexamination Request:
No. 90/002,072, Jun. 29, 1990

Reexamination Certificate for:

Patent No.:	**4,879,181**
Issued:	**Nov. 7, 1989**
Appl. No.:	**40,534**
Filed:	**Apr. 20, 1987**

Certificate of Correction issued Apr. 21, 1992.

Related U.S. Application Data

[60] Continuation of Ser. No. 712,909, Mar. 15, 1985, abandoned, and a continuation-in-part of Ser. No. 347,210, Feb. 9, 1982, abandoned, which is a continuation of Ser. No. 565,429, Dec. 27, 1983, abandoned, which is a division of Ser. No. 405,055, Aug. 4, 1982, Pat. No. 4,427,068, which is a continuation-in-part of Ser. No. 347,210, Feb. 9, 1982, abandoned.

[51] **Int. Cl.**^{5} **B32B 18/00; C09K 7/00**

[52] **U.S. Cl.** **428/402;** 252/8.551; 428/403; 501/127; 501/128

[58] **Field of Search** 428/402; 501/127, 128; 252/8.551

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,976,138 8/1976 Colpoys, Jr. et al. .

OTHER PUBLICATIONS

Oxide Ceramic Proppants for Treatment of Deep Well Fractures, SPE 6816, by E. A. Neel, J. L. Parmley, and P. J. Colpoys, Jr. (1977).

UCAR Ceramic Props, The Ideal Proppant for Deep Wells and High Compaction Pressures.

Primary Examiner—Jenna Davis

[57] **ABSTRACT**

Sintered, spherical composite pellets or particles comprising one or more clays as a major component and bauxite, alumina, or mixtures thereof, are described, along with the process for their manufacture. The pellets may have an alumina-silica (Al_2O_3—SiO_2) ratio from about 9:1 to about 1:1 by weight. The use of such pellets in hydraulic fracturing of subterranean formations is also described.

REEXAMINATION CERTIFICATE ISSUED UNDER 35 U.S.C. 307

NO AMENDMENTS HAVE BEEN MADE TO THE PATENT

AS A RESULT OF REEXAMINATION, IT HAS BEEN DETERMINED THAT:

The patentability of claims 1 to 14 is confirmed.

* * * * *

EXHIBIT 7

United States Patent [19]

Fitzgibbon

[11] **Patent Number: 4,623,630**

[45] **Date of Patent: Nov. 18, 1986**

[54] **USE OF UNCALCINED/PARTIALLY CALCINED INGREDIENTS IN THE MANUFACTURE OF SINTERED PELLETS USEFUL FOR GAS AND OIL WELL PROPPANTS**

[75] Inventor: **Jeremiah J. Fitzgibbon**, LaFayette, La.

[73] Assignee: **Standard Oil Proppants Company**, Dallas, Tex.

[21] Appl. No.: **538,058**

[22] Filed: **Sep. 30, 1983**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 405,055, Aug. 4, 1982, Pat. No. 4,427,068, which is a continuation of Ser. No. 347,210, Feb. 9, 1982, abandoned.

[51] **Int. Cl.^{4}** **C04B 35/10**

[52] **U.S. Cl.** **501/127**; 501/141; 501/33; 166/280

[58] **Field of Search** 501/29, 33, 127, 141; 166/271, 280, 305

[56] **References Cited**

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Primary Examiner—William R. Dixon, Jr.
Assistant Examiner—Steven Capella
Attorney, Agent, or Firm—David M. Ronyak

[57] **ABSTRACT**

A composite, sintered, spherical pellet and a method for its manufacture are described. The pellet comprises clay and a member of the group of bauxite, alumina, or mixtures thereof; the pellet being prepared from at least one uncalcined or partially calcined ingredient. The pellet may have an alumina-to-silica ratio from about 9:1 to about 1:1. The pellet has a specific gravity of less than 3.40. Use of such pellets in propping hydraulically fractured subterranean formations is also described.

26 Claims, No Drawings

USE OF UNCALCINED/PARTIALLY CALCINED INGREDIENTS IN THE MANUFACTURE OF SINTERED PELLETS USEFUL FOR GAS AND OIL WELL PROPPANTS

This is a continuation-in-part of Ser. No. 405,055, filed Aug. 4, 1982, now U.S. Pat. No. 4,427,068, which is a continuation-in-part of Ser. No. 347,210, filed Feb. 9, 1982, abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to oil and gas well proppants and, more particularly, to sintered proppants made from ingredients at least some of which are uncalcined or partially calcined, a method of making such proppants, and to a method of maintaining a fracture in a subterranean formation in a propped condition by utilizing such proppants.

2. History of the Prior Art

Oil and natural gas are produced from wells having porous and permeable subterranean formations. The porosity of the formation permits the formation to store oil and gas, and the permeability of the formation permits the oil or gas fluid to move through the formation. Permeability of the formation is essential to permit oil and gas to flow to a location where it can be pumped from the well. Sometimes the permeability of the formation holding the gas or oil is insufficient for economic recovery of oil and gas. In other cases, during operation of the well, the permeability of the formation drops to the extent that further recovery becomes uneconomical. In such cases, it is necessary to fracture the formation and prop the fracture in an open condition by means of a proppant material or propping agent. Such fracturing is usually accomplished by hydraulic pressure, and the proppant material or propping agent is a particulate material, such as sand, glass beads or ceramic pellets, which are carried into the fracture by means of a fluid.

Spherical pellets of uniform size are believed to be the most effective proppants due to maximized permeability. For this reason, assuming other properties to be equal, spherical or essentially spherical proppants, such as rounded sand grains, metallic shot, glass beads and tabular alumina, are preferred.

In practice, in deep wells, where high pressures are encountered, e.g., above about 700 kg/cm^2 (10,000 psi), the immediately foregoing specifically mentioned proppants are either entirely ineffective or do not exhibit desired permeability. Examples of prior art proppants and their use are found in U.S. Pat. Nos. 2,950,247, McGuire, et al; 3,026,938, Huitt, et al; 3,126,056, Harrell; 3,497,008, Graham, et al; 3,976,138, Colpoys, et al; and 4,068,718, Cooke, et al. One of the better proppants useful at high pressures, disclosed in U.S. Pat. No. 3,976,138, is predominantly alumina. However, even such alumina, as disclosed in U.S. Pat. No. 3,976,138, has reduced permeability at pressures in excess of 350 Kg/cm^2 (5,000 psi).

As disclosed in U.S. Pat. No. 4,068,718, sintered bauxite made from calcined bauxite unexpectedly has a permeability which is superior to the previously mentioned proppant materials at pressures as high as 700 kg/cm^2 (10,000 psi) or higher. Pellets having a high apparent specific gravity, i.e. greater than 3.4, are disclosed in U.S. Pat. No. 4,068,718 to be most suitable as proppant materials.

The prior art sintered bauxite particles made from calcined bauxite may be produced in spherical shape as described in R. J. Seider's commonly assigned, copending U.S. Patent Application Ser. No. 252,491, filed Apr. 8, 1981 abandoned, as a continuation of U.S. Patent Application Ser. No. 969,122, filed Dec. 13, 1978 abandoned. Such prior art sintered bauxite proppants prepared from fully calcined bauxite, although extremely useful under high pressure conditions, over about 700 kg/cm^2 (10,000 psi), are costly. The cost of the prior art high strength, sintered, calcined bauxite proppant for wells of intermediate pressures, between about 350 and 700 kg/cm^2 (5,000 and about 10,000 psi), may not be economically justified.

The manufacture of sintered spherical pellets from calcined clay and calcined bauxite, calcined alumina or mixtures thereof, is described in J. F. Fitzgibbon's commonly assigned, copending U.S. Patent Application Ser. Nos. 347,210 filed Feb. 9, 1982 abandoned, and 405,055 filed Aug. 4, 1982 now U.S. Pat. No. 4,427,068. These pellets are available at somewhat lower cost and are aptly suited to use under pressures of up to about 700 Kg/cm^2 (10,000 psi). These pellets have lower specific gravities and bulk densities than those made according to U.S. Pat. No. 4,068,718.

Calcining adds considerably to the cost of the raw materials or ingredients used in the manufacture of pellets useful as proppant. For example, the cost of dried diaspore clay is about 35 dollars per ton, if air dried. The cost of the same material is about 70 dollars per ton, if fully calcined.

While the prior art ceramic pellets made from fully calcined ingredients are aply suited for many proppant applications there remains a need to provide strong ceramic pellets that are of even lower cost.

The present invention provides strong pellets aptly suited to use as proppants under pressures of up to about 700 kg/cm^2 (10,000 psi), which are more economical than previously available synthetic ceramic proppants and have low specific gravities and bulk densities, which benefit the user, in that fewer pounds of proppant per cubic foot of fracture are required. Handling, e.g., pumping of slurries of low density material, is easier than handling of high density materials.

BRIEF DESCRIPTION OF THE INVENTION

In accord with the present invention, composite, spherical pellets or particles containing one or more uncalcined or partially calcined ingredients as a component and having an alumina-to-silica dry weight basis ratio of from about 9:1 to about 1:1 and apparent specific gravities less than 3.30, are produced. Diaspore clay, burley clay and flint clay have been found to be useful in the manufacture of such pellets although it is believed that other clays may be employed. Surinam and Comalco bauxites have been found to be useful although it is believed that other bauxites may be employed. Such spherical particles having an alumina to silica dry weight basis ratio of from about 9:1 to 1:1 and an apparent specific gravity of at least about 2.6 are useful as oil and gas well proppants.

The present uncalcined or partially calcined materials which are particularly adapted to use in combination with known, prior art proppant materials include fines from the dust collection systems of clay calcining kilns, and uncalcined or partially calcined clays and uncalcined or partially calcined bauxites. These uncalcined or partially calcined materials are blended with fully calcined clays and fully calcined bauxites or alumina to produce composite sinterable, spherical pellets which are subsequently furnaced to produce sintered, spherical pellets eminently useful as proppants. The composites of the present invention may be made from a significant portion and may even be made from a major portion of an uncalcined or partially calcined ingredient or ingredients. Composites of the present invention may be made from a very small amount of uncalcined or partially calcined ingredients but preferably are made from at least about five (5) percent by weight of uncalcined or partially calcined ingredients.

The partially calcined and uncalcined clay and bauxite materials of the present invention are compatible with, and may be formed into a matrix with, a wide variety of proppant materials, and, in this manner, a wide variety of composite proppants may be produced, which may be customized to particular conditions or formations. Thus, the properties of the final sintered composite pellets, such as strength, permeability, specific gravity, bulk density and acid resistance, may be controlled through variations in the initial component mixture.

Combinations of dust collector fines, diaspore clay and bauxite are particularly useful. Such mixtures may suitably contain up to 70 percent by weight uncalcined clay. Mixtures containing up to 50 percent by weight uncalcined clay have a broad range of use, and mixtures containing up to 40 percent by weight uncalcined clay have a particularly broad range of use.

The present invention also provides a process for propping fractures in oil and gas wells at depths of 6,000 to 14,000 feet utilizing the present sintered pellets by mixing the pellets with a fluid, such as oil or water, and introducing the mixture into a fracture in a subterranean formation. The compaction pressure upon the fracture generally is at least 280 kg/cm^2 (4,000 psi) and usually is in the range of from about 350 to about 700 kg/cm^2 (5,000 to about 10,000 psi). The present pellets have an average particle size between 0.1 and 2.5 millimeters. It has been found that the present composite pellets containing 50 percent or more parts by weight uncalcined clay, at pressures up to about 700 kg/cm^2 (10,000 psi), have desirable permeability characteristics, i.e., they exhibit a permeability to brine at about 93.3° C. (200° F.) which decreases not more than about three-fourths when the pressure applied to them is increased from 140 to 700 kg/cm^2 (2,000 to 10,000 psi).

The present proppant materials are produced by forming a mixture of dried but uncalcined or only partially calcined clays and bauxites and dust collector fines with fully calcined materials. The starting ingredients have an average particle size of less than about 15 microns and, preferably, less than about 10 microns and, most preferably, less than about 5 microns.

In a preferred method, the mixture is produced on an intensive mixer having a rotatable table provided with a rotatable impacting impeller, such as described in U.S. Pat. No. 3,690,622, to Brunner. Sufficient water is added to cause essentially spherical ceramic pellets to form, and, after such pellets have formed, from about 5 to about 15 percent of additional ceramic powder by weight of pellets is added, and the mixer is further operated to cause accretion of the added material to the pellets being formed.

The resulting pellets are then dried to a moisture content of less than ten (10) weight percent, usually at between about 100 and about 300 degrees centigrade, and thereafter furnaced at sintering temperature until an apparent specific gravity between about 2.60 and about 3.30 is obtained, depending on the composition of the sintering mixture.

DETAILED DESCRIPTION OF THE INVENTION

The sintered composite proppant pellets of the present invention have apparent specific gravities less than 3.30. Preferably they spherical in shape.

The sphericity of the pellets may be determined using a visual comparator. Krumbein and Sloss, *Stratigraphy and Sedimentation*, second edition, 1955, W. H. Freeman & Co., San Francisco, CA, describe a chart for use in visual determination of sphericity and roundness. Visual comparison using this chart is a widely used method of evaluating sphericity or roundness of particles. In using the visual comparison method, a random sample of 10 to 20 particles of the material to be tested is selected. The particles are viewed under a 10 to 20 power microscope or photomicrograph and their shapes compared to the Krumbein and Sloss chart. The chart values for sphericity range from 0.3 to 0.9. The chart values for the individual particles are then averaged to obtain a sphericity value. The present particles have an average sphericity of about 0.7 or greater when visually compared with the Krumbein and Sloss chart.

"Spherical" and related forms, as used herein, is intended to mean an average ratio of minimum diameter to maximum diameter of about 0.70 or greater, or having an average sphericity value of about 0.7 or greater compared to a Krumbein and Sloss chart.

"Bulk density", as used herein, is the weight per unit volume, including in the volume considered, the void spaces between the particles.

"Apparent specific gravity" is a number without units, but numerically equal to the weight in grams per cubic centimeter of volume, excluding void space or open porosity in determining the volume. The apparent specific gravity values given herein were determined by liquid (ethylbenzene) displacement.

"Theoretical density" and "true specific gravity" exclude not only the void space between particles and open porosity of particles from the volume, but also exclude closed porosity. These latter two measures are not customarily used for characterizing proppants. Theoretical density and true specific gravity require fine grinding to expose any closed porosity.

"Calcined" as used herein, refers to a process to which a material has been subjected. Ore materials that have been fully subjected to calcination or a calcining process exhibit very low loss on ignition (LOI) and moisture contents, e.g. about 1-2 percent by weight or less. Uncalcined ore materials such as bauxites and clays can contain from about 10 to about 40 percent by weight volatiles. "Partially calcined" materials such as diaspore clay calcination kiln dust collection system fines typically exhibit total volatiles (LOI plus moisture content) of 5 to 8 percent by weight. Volatiles can include moisture, organics and chemically held water (eg water of hydration).

"Dust collector fines" as used herein refers to material obtained from the dust collection system of a calcining kiln operating on a clay or bauxite ore. Such fines are usually partially calcined and exhibit a higher silica (SiO_2) content than the ore being processed in the kiln.

Unless otherwise stated at the point of interest, all percentages, proportions and values with respect to composition are expressed in terms of weight.

The sintered, spherical pellets of the present invention may be manufactured by furnacing a mixture of calcined and partially calcined or uncalcined ingredients. While various sintering aids, such as bentonite clay or iron oxide, boron, boron carbide, aluminum diboride, boron nitride, boron phosphide and other boron compounds, and fluxes, such as sodium carbonate, lithium carbonate, feldspar, manganese oxide, titania, iron oxide and sodium silicates, may be added in amounts up to about ten (10) weight percent to aid sintering, such additions are generally unnecessary because the use of partially or totally uncalcined ingredients promotes sintering at lower temperatures than those necessary to obtain finished pellets having comparable properties when using only fully calcined ingredients. If desired, a binder, for example, various resins or waxes known in the prior art, may be added to the initial mixture to improve pelletizing and to increase the green strength of the unsintered pellets.

Pellets according to the present invention and for use with the present invention may be prepared from a mixture of any of the clays described in Tables I and II with one or more bauxites or alumina or mixtures of these. The composition of specific bauxites employed in the manufacture of the pellets described herein is also given in Tables I and II. All values in Tables I and II are expressed as percentages by weight. Where an omission occurs, it indicates that sufficient testing was not conducted to obtain a value.

TABLE I

(Typical Analysis of Ingredients)

	Surinam Bauxite	Control Batch	Uncalcined Clay (16 Mesh and Finer)	Uncalcined Clay (1982 Stockpile)	Uncalcined Clay (Stockpile #1)	(Dust Collector Fines) Samp. 1	Samp. 2	Samp. 3	Samp. 4
H_2O	0.57	.611	0.88	0.88	0.81	—	—	—	1.51
LOI	1.23	1.26	11.12	11.12	12.75	6.20	6.27	6.07	6.51
Al_2O_3	86.96	71.6	51.84	51.84	58.53	45.52	45.44	47.33	58.41
SiO_2	2.51	16.929	37.87	37.87	29.53	41.00	41.08	39.76	26.18
Fe_2O_3	5.95	4.84	1.04	1.04	1.00	2.30	2.29	2.49	3.34
TiO_2	3.35	3.06	2.65	2.65	3.09	4.08	4.06	4.28	4.05
Na_2O	—	1.32	.021	.021	.009	1.41	1.37	1.91	—
K_2O	—	.94	4.25	4.25	2.82	0.055	0.017	0.049	—
CaO	—	.08	0.14	0.14	0.15	1.42	1.42	1.30	—

TABLE II

(Typical Analysis of Ingredients - calcined)

Chemical Compound	Surinam Bauxite	High Purity Dis- apore Clay	High Silica Dis- apore Clay	High Iron (Brown) Disapore Clay	Burley Clay	Flint Clay
Al_2O_3	86.80	75.10	70.00	78.30	54.07	38.52
SiO_2	3.42	18.60	24.40	15.09	41.33	56.64
Fe_2O_3	4.74	0.80	0.80	2.63	1.26	0.65
TiO_2	3.13	2.99	3.04	3.05	2.45	3.49
Other (e.g. MgO, CaO)	1.00	1.51	—	0.72	0.74	0.67
Loss on Ignition Moisture	0.91	1.00	—	0.21	0.15	0.03
Apparent 2.5–2.6 Specific Gravity After Calcining	3.6–3.7	2.9–3.1	2.9–3	2.9–3.1	2.7–2.8	

TABLE II-continued

(Typical Analysis of Ingredients - calcined)

Chemical Compound	Surinam Bauxite	High Purity Dis- apore Clay	High Silica Dis- apore Clay	High Iron (Brown) Disapore Clay	Burley Clay	Flint Clay
g/cc						

Each of the clays and dust collector fines described in Tables I and II may be obtained from Missouri Minerals Processing, High Hill, Mo. 63350, in raw or calcined form.

The Surinam bauxite described in Table I may be obtained from Aluminum Company of America, Pittsburgh, Pa. 15219. Surinam bauxite is so designated for that is the country in which it is mined. It is expected that other bauxites may be used without departing from the present invention.

Diaspore clays, as found in nature, are predominantly hydrated aluminum oxide ($Al_2O_3.H_2O$). Such clays occur in emery rock in association with corundum. The main deposits of diaspore clays in the United States are in Missouri and Pennsylvania. Diaspore clays have a hardness between 6.5 and 7.0 and a true specific gravity usually between 3.30 and 3.45 gm/cm^3. The crystal structure of diaspore clay is orthorhombic. Typically, diaspore clay, as found in nature, contains 25 to 30 percent by weight, and, in some cases, as high as 35 percent by weight, of impurities. Generally, the major impurities are: SiO_2, which typically ranges from about 12 to about 25 percent by weight; TiO_2, which typically ranges from about 2.75 to 3.75 percent; Fe_2O_3, typically between 0.25 and 1.0 percent, and MgO and CaO, generally less than 1.0 percent.

Dust collector fines sample 4 was generated while calcining diaspore clay. The materials which were being calcined during generation of dust collector fines samples 1–3 are not known.

The uncalcined clay and bauxitic materials for use in the present invention are usually air dried at low temperature, e.g. 90°–150° C. (200°–300° F.) prior to use with other calcined ingredients. Air drying removes free moisture; that is, moisture that is not chemically combined. The calcined ingredients are initially calcined, by known prior art methods, at temperatures and times sufficiently high, typically 1000°–1200° C., to remove any organic material and to remove most or all water of hydration. Water of hydration is chemically combined water. Calcined and partially calcined materials may be used without further treatment unless they have been stored in a manner that permits pickup of free moisture, in which circumstance they should be dried in air or at low temperature prior to use. Free water or moisture is not chemically combined. Excess free moisture may cause agglomeration and caking during ball milling of the ingredients. Ball milling is normally employed to reduce the particle size of the ceramic ingredients the desired small size.

The sintered pellets of the present invention are preferably made as follows:

1. Starting ingredients of uncalcined or partially calcined clay and calcined clay and uncalcined or partially calcined bauxite and calcined bauxite or alumina, or mixtures thereof, are added in a predetermined ratio to a high intensity mixer. The ratio of ingredients is chosen based on analysis of the ingredients and desired analysis and specific gravity of the pellets to be produced. Preferably, at least five (5) percent of the total ingredients on a dry weight basis is uncalcined or partially calcined material. Each of the ceramic ingredients has an average particle size of less than about 15 microns and preferably less than about 10 microns and most preferably, less than about 5 microns.

Small particle size is required in order to obtain a finished spherical sintered pellet having the desired density. An average particle size of smaller than 5 microns is desirable, and the average particle size is most preferably below 3 microns and usually above 0.5 microns.

2. The powdered ceramic starting ingredients are stirred to form a dry homogeneous particulate mixture having an average particle size of less than about 15 microns.

A preferred stirring or mixing device is that obtainable from Eirich Machines, Inc., known as the Eirich Mixer. A mixer of this type is provided with a horizontal or inclined circular table, which can be made to rotate at a speed of from about 10 to about 60 revolutions per minute (rpm), and is provided with a rotatable impacting impeller, which can be made to rotate at a tip speed of from about 5 to about 50 meters per second. The direction of rotation of the table is opposite that of the impeller, causing material added to the mixer to flow over itself in countercurrent manner. The central axis of the impacting impeller is generally located within the mixer at a position off center from the central axis of the rotatable table. The table may be in a horizontal or inclined position, wherein the incline, if any, is between 0 and 35 degrees from the horizontal.

3. While the mixture is being stirred, there is added sufficient water to cause formation of composite, spherical pellets from the ceramic powder mixture.

In general, the total quantity of water which is sufficient to cause essentially spherical pellets to form is from about 17 to about 20 percent by weight of the initial starting ceramic ingredients and usually between about 18 and about 20 percent by weight of the initial ceramic powder. The total mixing time usually is from about 2 to about 6 minutes.

After the clay mixture is added to the mixer, the table is rotated at from about 10 to about 60 rpm and, preferably, from about 20 to about 40 rpm, and the impacting impeller is rotated to obtain a tip speed of from about 25 to about 50, preferably, from about 25 to about 35, meters per second, and sufficient water is added to cause essentially spherical pellets of the desired size to form. If desired, the impeller may be initially rotated at a lower tip speed of from about 5 to about 20 meters per second during addition of the first half of the sufficient water and subsequently rotated at the higher tip speed of 25 to about 50 meters per second during the addition of the balance of the water. The rate of water addition is not critical. The intense mixing action quickly disperses the water throughout the particles.

4. The resulting pellets are dried at a temperature well below sintering temperature until less than 10 percent, preferably less than 3 percent and, most preferably, less than 1 percent free moisture remains in the pellets. Drying is preferably done in a rotary kiln with flowing gas at a temperature of between about 100° (212° F.) and about 300° C. (572° F.). The most preferred drying gas temperature is between about 175° (347° F.) and 275° C. (527° F.), and the drying time required is usually between about 30 and about 60 minutes. The pellets themselves are generally at a lower temperature than that of the heated gas used to dry them.

5. The dried pellets are then furnaced at sintering temperature for a period sufficient to enable recovery of sintered, spherical pellets having an apparent specific gravity of between 2.70 and 3.30 and a bulk density of from about 1.35 to about 1.80 grams per cubic centimeter. The specific time and temperature to be employed is, of course, dependent on the ingredients employed and the optimum time and temperature for a given starting composition is determined empirically according to the results of physical testing of the resulting pellets after furnacing.

The furnacing step is carried out to sinter the composite pellets; generally, temperatures of between about 1,300° C. (2,372° F.) and about 1,500° C. (2,732° F.) for about 4 to about 20 minutes and, more preferably, from about 1,375° (2,498° F.) to about 1,435° C. (2,606° F.) for about 4 to about 8 minutes, are useful, depending upon the sintering aids and fluxes which may be included or naturally present in the ingredients.

While the process just described hereinabove will yield pellets according to the invention, it is preferred that from about 5 to about 15 percent and, preferably, from about 8 to about 10 percent of additional starting ingredients by weight of pellets be added, after the addition of water but prior to drying of the pellets. The added material is usually but not necessarily of the same composition as that described in step 1. For example, the added material may be pure calcined bauxite or alumina when starting ingredients include uncalcined or partially calcined bauxites and/or clays; thus the composition of the pellets may vary with radius. The addition of more dry ceramic powder is followed by rotating the impeller at a tip speed of between about 5 and about 20 meters per second, preferably, between about 10 and about 20 meters per second, for from about 1 to about 6 minutes, while continuing to rotate the table at from about 10 to about 60 rpm and, preferably, from about 20 to about 40 rpm. This step improves yield and results in improved sphericity of the pellets.

If desired, the rotation of the impeller may then be stopped while the table continues to rotate for between about 1 and about 5 minutes.

The impacting impeller is preferably a disk provided with peripheral rods or bars attached to the disk. The longitudinal axis of the rods or bars is desirably essentially parallel with the axis of rotation of the impeller, which is usually a vertical axis. The diameter of the impeller is measured from the axis of rotation to the center of the most distant rod or bar. Tip speed is the speed of the most distant rod or bar.

The diameter of the impeller depends upon the size of the mixer but is usually slightly less than 25 percent of the diameter of the mixer. The impeller in most applications is between 10 and 100 centimeters in diameter and usually rotates at from 200 to 3,750 rpm at the lower tip speeds of 10 to 20 meters per second, depending upon impeller diameter, and at from 500 to 6,500 rpm at the higher tip speeds of 25 to 35 meters per second, depending upon impeller diameter.

The pellets are screened for size, preferably after drying. However, they may be screened before drying or after furnacing. The rejected oversized and undersized pellets and powdered material obtained after the drying and screening steps may be recycled. The finished pellets may be tumbled to enhance smoothness. The resultant sintered pellets have a bulk density ranging from about 1.35 to about 1.80 grams per cubic centimeter, depending upon the ceramic starting ingredients employed.

The overall particle size of the pellets recommended for use as propping agent for increasing permeability in a subterranean formation penetrated by well is between 0.1 and about 2.5 millimeters and preferably between about 0.15 and 1.7 millimeters.

EXAMPLE 1

The pellets which may be produced according to this example correspond to those identified as Sample No. 1 in Table III. About 81 kilograms of diaspore clay material that had been previously calcined at a temperature sufficiently high to remove any organic materials and substantially all of the water of hydration from the clay, together with about 54 kilograms of bauxite (60 percent by weight calcined clay 40 percent by weight calcined bauxite) powder having an average particle size of between 4 and 8 microns is added to an Eirich mixer having a table diameter of about 115 centimeters, an operating capacity of about 160 kilograms and an impacting impeller diameter of about 27 centimeters.

The table is rotated at about 35 rpm, and the impeller is rotated at about 1,090 rpm, and about 27 kilograms of water is added. Rotation of the table and impeller is continued for about 1 minute; subsequently, the impeller speed is increased to about 2,175 rpm. The table and impeller is rotated until seed pellets are formed, less than 5 percent of which being of a size smaller than 0.50 mm (about 3 minutes). The impeller is then reduced to about 1,090 rpm, and about 4.08 kilograms of the initial diaspore clay—bauxite powder mixture is added. Rotation of the pan and impeller is then continued for an additional 2 minutes to form spherical pellets.

The pellets are then dried for about 20 minutes at about 110° C. (230° F.) in a rotary dryer and then fired at about 1,480° C. (2,696° F.) for about 5 minutes to sinter them. The yield of useful pellets having a size between 150 and 1,700 microns (0.15 and 1.7 millimeters) is typically greater that 80 percent by weight of starting ceramic powder. The resulting pellets have an apparent specific gravity of about 3.27, a bulk density of 1.79 gm/cm^3 and a sphericity of greater than 0.7, as determined using the Krumbein and Sloss chart. These pellets are identified as Sample No. 1 in the accompanying Table III.

The pellets identified as Sample Nos. 2–29 in Table III were prepared in a manner comparable to that given in Example I except for the use of different ingredients and proportions and sintering temperatures.

In accompanying Table III is summarized the results of testing for several different pellets according to the invention which were produced from the raw materials

in the proportions indicated. Unless otherwise indicated, parts and percentages are by weight. All samples were prepared in accord with the procedures given herein. Example 1 gives in detail the procedure employed in the preparation of Sample No. 1, which procedure is typical of that employed in preparation of the remainder of the samples reported in Table III.

The test procedures and apparatus employed to test the permeability in darcies of the pellets of the present invention including placing a predetermined quantity of the material to be tested between two parallel hardened steel plates, applying force tending to close the initially established 0.125 inch gap between the plates, then measuring the flow rate through the packed cell using distilled water at room temperature at various applied stresses or pressures. The particle size distribution of the pellets was 20×40 mesh, U.S. Standard Sieve (ninety percent by weight minimum of pellets will pass through 20 mesh [841 micron] screen but not through 40 mesh [420 micron] screen).

Values obtained using the American Petroleum Institute (API) procedure for determining resistance to crushing are also reported in Table III. According to this procedure, a bed of about 6 mm depth of sample to be tested is placed in a hollow cylindrical cell. A piston is thereafter inserted in the cell. Thereafter, a load is applied to the sample via the piston. One minute is taken to reach maximum load which is then held for two minutes. The load is thereafter removed, the sample removed from the cell, and screened to separate crushed material. The results are reported as the weight percentage the original sample that crushed. This crushed material is referred to in Table III as "percent fines generated."

Single Pellet Crush is another procedure useful in determining the resistance of pellets to an applied load. In this procedure the pellets of a given sample are first separated into size fractions by sieving. United States Standard Sieves were employed for the data reported in Table III. Thereafter, for each size fraction a quantity, eg. about twenty (20), of the individual pellets are measured and recorded. Each individual pellet is thereafter placed between two flat, hardened parallel plates which are mounted in a press. A load is thereafter applied to the plates. The amount of load required to crush a specific pellet is noted. Results are reported as the arithmetic average value obtained within each size fraction of a given pellet sample for the amount of applied load (pounds force) divided by the diameter-in-inches squared for each of the individual pellets tested (load/-diameter squared). The use of ceramic plates is recommended to minimize wear of the testing apparatus.

Carborundum Crush is another procedure for determining the resistance of pellets to an applied load. In this procedure a steel die having a cylindrical cavity of one and one-eighth inch diameter (one square inch area) is filled 10 grams of the pellets to be tested. Thereafter a right cylindrical plunger closely corresponding in diameter to that of the die is inserted into the die and loaded by manually pumping a hydraulic press. The results are reported as the amount of compression (original unloaded pellet column height minus loaded pellet column height) versus applied load. The amount of compression is expressed in thousandths of an inch. The load is expressed in psi.

Acid solubility of the samples reported in Table III was tested in accordance with recommended API test procedure, fourth draft, June 1980. In this procedure a known weight of sample (5 g) is placed in a 150 ml polyethylene beaker containing 100 ml of a combined acid solution containing 12 percent HCl acid and 3 percent HF acid. The sample-and-acid-containing beaker is then placed in a 65.6° C. (150° F.) water bath for 30 to 35 minutes. The sample is not stirred. The sample is thereafter filtered through a previously weighed filter crucible or funnel and washed three times with 20 ml portions of distilled water. The filtered and washed sample is thereafter dried to constant weight (approximately one hour) at 105° C. (220° F.). The values given in Table III represent the percentage of weight lost or dissolved due to the acid.

Sphericity of the pellets reported in Table III was determined using a Krumbein and Sloss chart. The values reported represent an average of 10–20 pellets per sample.

Roundness as reported in Table III is a measure of the relative sharpness of the pellet corners, or of curvature. This evaluation may he done at the same time and on the same sample as that used for sphericity. The pellets are visually compared with a Krumhein and Sloss chart. The values reported represent an average of 10–20 pellets per sample.

Bulk density values reported in Table III were determined by weighing that amount of sample that would fill a cup of known volume.

TABLE III

		SAMPLE NO.						
		1	2	3	4	5	6	7
		COMPOSITION						
		60% Calcined Diaspore Clay 40% Calcined Bauxite	Sintered Calcined Bauxite	4% D.C. Fines 76% Calcined Clay 20% Calcined Bauxite	D.C. Fines 72% Calcined Clay 20% Calcined Bauxite	60% Calcined Clay 10% Dust Collector Fines 30% Calcined Bauxite	50% Calcined Clay 10% Dust Collector Fines 40% Calcined Bauxite	70% Dust Collector Fines 30% Calcined Bauxite
SINTERING TEMP. (C.°)		1480	1495	1435	1410	1480	1400-1500	
ROUNDNESS		0.86	0.82	—	0.78	0.78	0.81	Repeat Samples Failed Initial Strength Qualification Tests Very Poor Product
SPHERICITY		0.85	0.87	—	0.79	0.80	0.81	
ACID SOLUBILITY (12-3)		5.42	1.60	7.09	6.92	6.33	5.11	
BULK DENSITY	(g/cc)	1.79	2.05	1.62	1.64	1.71	1.67	
	(pcf)	112	128	101	102	107	104.00	
ASG (g/cc)		3.27	3.58	3.05	3.02	3.05	3.02	
API CRUSH	(7500 psi)	—	—	—	—	—	—	
(% weight of fines generated)	(10000 psi)	9.9	3.8	8.4	7.50	7.42	7.19	
SINGLE PELLET	(−16/+20)	—	26542	25974	22852	—	23427	
CRUSH	(−20/+25)	30903	28990	22481	25415	—	24158	
	(−25/+30)	31021	—	27985	28757	—	27365	
	(−30/+35)	34011	34250	30319	30604	—	28703	
	(−35/+40)	30827	33379	—	34717	—	30599	
PERMEABILITY	2000	225	229	—	214	235		
(Darcies)	4000	192	208	—	194	210		
at	6000	162	188	—	166	180		
Applied	8000	136	165	—	135	140		
Pressure	10000	110	144	—	99	104		
(psi)	12000	86	123	—	76	82		
	14000	64	102	—	62	66		
CARBO CRUSH	0.010 inch							
(force	0.020 inch							
applied in	0.030 inch							
lbs × 1000	0.040 inch							
to induce	0.050 inch							
specified	0.060 inch							
deflection)	0.070 inch							

		SAMPLE NO.																		
		8				9				10			11				12			
		COMPOSITION																		
		Control Batch (Refer to Table I)				Control Batch (Refer to Table I)				5% Dust Collector Fines Remainder Control Batch Material			5% Uncalcined Clay Addition (1982 Stockpile) Remainder Control Batch Material				5% Uncalcined Clay Addition (1982 Stockpile) Remainder control Batch Material			
SINTERING TEMP. (C.°)		1465	1480	1495	1510	1465	1480	1495	1510	1480	1495	1510	1465	1485	1495	1510	1465	1485	1495	1510
ROUNDNESS																				
SPHERICITY																				
ACID SOLUBILITY (12-3)					3.89															
BULK DENSITY	(g/cc)																			
	(pcf)																			
ASG (g/cc)		3.20	3.22	3.22	3.22	3.20	3.21	3.21	3.21	3.10	3.09	3.10	3.14	3.12	3.12	3.13	3.14	3.13	3.13	3.13
API CRUSH	(7500 psi)																			

TABLE III-continued

(% weight	(10000 psi)	7.00	6.02	4.69	5.26	7.90	6.06	3.96	4.25	7.45	6.77	5.98	10.32	9.86	8.34	7.34	8.43	7.01	6.75	6.50
of fines generated)																				
SINGLE PELLET	(−16/+20)																			
CRUSH	(−20/+25)																			
	(−25/+30)																			
	(−30/+35)																			
	(−35/+40)																			
PERMEABILITY	2000																			
(Darcies)	4000																			
at	6000																			
Applied	8000																			
Pressure	10000																			
(psi)	12000																			
	14000																			
CARBO CRUSH	0.010 inch	1.4	1.8	2.0	2.0	1.4	2.0	2.2	2.0	2.0	2.0	2.4	1.6	2.0	2.0	2.2	2.0	2.4	2.6	2.6
	0.020 inch	2.8	4.0	4.8	4.0	2.8	4.2	5.0	5.0	4.6	5.0	6.2	4.2	4.6	5.6	6.2	5.5	6.4	5.6	5.8
	0.030 inch	6.6	9.0	9.8	8.4	6.6	9.6	10.2	9.6	10.2	10.8	11.2	8.0	8.6	9.4	10.2	8.0	10.4	10.4	10.4
	0.040 inch	10.4	14.2	14.6	14.6	10.4	14.2	15.2	14.8	14.0	14.8	15.6	11.6	12.4	13.0	13.8	11.6	13.8	14.0	14.2
	0.050 inch	14.2	18.4	18.6	18.0	14.2	18.6	19.0	18.4	17.8	18.4	20.0	19.6	15.4	16.8	17.2	14.6	17.6	18.6	18.6
	0.060 inch	18.0	23.2	23.6	21.6	18.0	23.6	24+	22.8	20.8	22.4	24.0	17.4	18.2	19.2	20.2	18.0	20.8	22.8	22.6
	0.070 inch	21.0	24.0	24.0	23.4	21.0	24+	—	24+	22.8	24.0+	—	20.4	21.6	22.0	23.0	21.8	23.2	24+	24+

		SAMPLE NO.																		
		13				14			15			16	17				18			
		COMPOSITION																		
		5% Uncalcined Clay Addition (1982 Stockpile) Remainder Control Batch Material				5% Uncalcined Clay Addition (16 Mesh and Finer) Remainder Control Batch Material			5% Uncalcined Clay Addition (16 Mesh and Finer) Remainder Control Batch Material			10% Uncalcined Clay Addition (1982 Stockpile) Remainder control Batch Material	15% Uncalcined Clay Addition (1982 Stockpile) Remainder Control Batch Material				20% Uncalcined Clay Addition (1982 Stockpile) Remainder Control Batch Material			
SINTERING TEMP. (C.°)		1465	1485	1495	1510	1465	1480	1495	1465	1480	1495	1495	1465	1480	1495	1510	1465	1480	1495	1510
ROUNDNESS																				
SPHERICITY																				
ACID SOLUBILITY (12-3)																				
BULK DENSITY	(g/cc)																			
	(pcf)																			
ASG (g/cc)		3.14	3.13	3.12	3.13	3.15	3.13	3.13	3.16	3.14	3.14	3.11	3.09	3.08	3.09	3.09 3.08	3.04	3.04	3.04	
API CRUSH	(7500 psi)																			
(% weight	(10000 psi)	10.7	7.16	6.85	6.34	10.1	8.35	8.49	11.8	9.86	9.95	7.88	9.55	8.26	7.59	6.72	10.12	8.76	7.83	7.56
of fines generated)																				
SINGLE PELLET	(−16/+20)																			
CRUSH	(−20/+25)																			
	(−25/+30)																			
	(−30/+35)																			
	(−35/+40)																			
PERMEABILITY	2000																			
(Darcies)	4000																			
at	6000																			
Applied	8000																			
Pressure	10000																			
(psi)	12000																			

TABLE III-continued

	14000																	
CARBO CRUSH	0.010 inch	2.0	2.0	2.4	2.2	2.0	2.2	2.4	2.0	2.0	2.0	1.6	1.8	2.0	2.0	2.0	1.8	2.2
(force	0.020 inch	5.0	5.2	6.0	6.2	5.0	5.4	5.0	5.0	4.4	4.6	4.0	3.8	5.0	5.0	5.2	3.4	5.0
applied in	0.030 inch	8.6	9.2	10.0	10.4	8.0	9.0	9.0	6.8	7.4	8.0	7.4	8.0	10.0	10.2	10.2	8.0	10.2
lbs × 1000	0.040 inch	11.6	12.7	14.0	14.6	10.6	12.0	16.8	9.6	10.2	10.6	10.4	11.0	13.2	13.6	14.6	11.4	13.2
to induce	0.050 inch	15.0	15.8	17.6	18.4	13.0	15.0	16.0	11.6	12.6	12.8	14.8	14.4	17.0	17.4	19.0	13.8	17.0
specified	0.060 inch	17.6	18.4	21.8	23.2	15.0	18.0	19.2	14.0	15.0	15.4	17.8	17.0	20.0	21.0	22.8	17.4	19.6
deflection)	0.070 inch	21.2	22.8	24+	24+	19.0	22.0	22.8	17.0	19.2	19.8	21.8	20.6	24+	24+	24+	20.6	23.2

		SAMPLE NO.																		
		19				20				21			22			23			24	
		COMPOSITION																		
		30% Uncalcined Clay Addition (1982 Stockpile) Remainder Control Batch Material				40% Uncalcined Clay (1982 Stockpile) 60% Calcined Bauxite				52% Uncalcined Clay (Stockpile #1) 50% Calcined Bauxite			50% Uncalcined Clay (Stockpile #1) 50% Calcined Bauxite			50% Uncalcined Clay (Stockpile #1) 50% Calcined Bauxite			60% Uncalcined Clay (Stockpile #1) 40% Calcined Bauxite	
SINTERING TEMP. (C.°)		1465	1480	1495	1510	1450	1465	1480	1495	1450	1465	1480	1450	1465	1480	1440	1450	1465	1450	1465
ROUNDNESS																				
SPHERICITY																				
ACID SOLUBILITY (12-3)										4.35										
BULK DENSITY	(g/cc)																			
	(pcf)																			
ASG (g/cc)		3.03	2.98	2.99	2.97	3.11	3.09	3.09	3.09	3.17	3.17	3.15	3.13	3.11	3.09	3.14	3.13	3.11	3.00	3.00
API CRUSH	(7500 psi)																			
(% weight	(10000 psi)	11.98	8.61	8.50	9.04	6.72	7.00	8.26	8.78	9.65	8.20	7.45	10.52	7.60		8.98	7.41	6.90	12.14	14.21
of fines generated)																				
SINGLE PELLET	(−16/+20)																			
	(−20/+25)																			
	(−25/+30)																			
	(−30/+35)																			
	(−35/+40)																			
PERMEABILITY	2000																	260		
(Darcies)	4000																	224		
at	6000																	189		
Applied	8000																	153		
Pressure	10000																	117.3		
(psi)	12000																	81.5		
	14000																	45.7		
CARBO CRUSH	0.010 inch	3.2	4.0	4.0	5.0		2.6	2.2					3.3	3.1					2.7	2.3
(force	0.020 inch	7.0	8.2	8.0	10.0		5.6	4.8					6.1	5.8					5.3	4.7
applied in	0.030 inch	10.0	11.1	11.0	14.0		11.2	10.0					8.8	8.4					7.4	6.5
lbs × 1000	0.040 inch	12.6	13.8	14.0	17.2		14.6	13.0					11.7	10.4					9.6	8.9
to induce	0.050 inch	14.6	16.2	16.4	20.6		17.8	17.4					14.9	13.9					12.2	11.3
specified	0.060 inch	16.6	20.6	20.0	23.0		21.2	19.4					18.6	16.9					14.8	7.4
deflection)	0.070 inch	20.6	23.2	23.8	24+		24+	22.8					21.7	19.8					17.9	17.0

SAMPLE NO.	
25	26
COMPOSITION	
60% Uncalcined Clay (Stockpile #1)	Uncalcined Clay (Stockpile #1) 30% Calcined

TABLE III-continued

		40% Calcined Bauxite				Bauxite		
SINTERING TEMP. (C.°)		1450	1400	1370	1350	1440	1450	1460
ROUNDNESS								
SHPERICITY								
ACID SOLUBILITY (12-3)								
BULK DENSITY	(g/cc)	1.52	1.59	1.66	1.75			
	(pcf)							
ASG (g/cc)		2.82	2.88	3.06	3.08	2.92	2.93	2.80
API CURSH	(7500 psi)							
(% weight	(10000 psi)	15.32	12.4	8.70	9.29	11.78	11.58	14.71
of fines generated)								
SINGLE PELLET	(−16/+20)							
	(−20/+25)							
	(−25/+30)							
	(−30/+35)							
	(−35/+40)							
PERMEABILITY	2000			249				
(Darcies)	4000			219				
at	6000			189				
Applied	8000			159				
Pressure	10000			130				
(psi)	12000			100				
	14000			70				
CARBO CRUSH	0.010 inch							
(force	0.020 inch							
applied in	0.030 inch							
lbs × 1000	0.040 inch							
to induce	0.050 inch							
specified	0.060 inch							
deflection)	0.070 inch							

Referring to Table III, Sample Nos. 1 and 2 may be used as baselines for comparison with pellets prepared according to the invention. Sample No. 1 was prepared from 60 percent calcined diaspore clay and 40 percent calcined bauxite and is considered to be an intermediate strength product suitable for use in wells down to a depth of about 14,000 feet, which corresponds to pressures of about 700 kg/cm^2 (10,000 psi). Sample 2 was prepared from calcined bauxite and is considered to be a premium high strength product suitable for use in wells of a depth exceeding 14,000 feet. Sample No. 2 is the standard against which other products including other standards such as Sample No. 1 are compared.

Samples Nos. 8 and 9 were prepared from a control batch of calcined clay and bauxite ingredients having the analysis indicated in Table 1. The control batch material is standard employed to assure that processing conditions are being maintained. The chemical composition of the control batch is similar to that of Sample No. 1, Table III.

Samples Nos. 3-7 and 10-26 of Table III were prepared utilizing at least one uncalcined or partially calcined ingredient.

The data given in Table III with respect to Sample Nos. 3, 4, 5, 6, 10 when compared with Sample No. 1 supports a conclusion that Sample Nos. 3, 4, 5, 6, 10 made from ingredients, including dust collector fines, are suitable as intermediate strength proppants. It is notable that the apparent specific gravity of Sample Nos. 3-6 and 10 are lower than that of Control Sample Nos. 1 and 8-9, yet the resistance-to-crushing as directly indicated by any of the crush resistance test results or indirectly indicated by the permeability test results of Sample Nos. 3-6 and 10 are comparable to that of the controls.

Sample No. 7 was prepared using 70 percent dust collector fines. This product was unsatisfactory and crushed easily.

Samples Nos. 11-15 were each prepared from the same ratio and type of ingredients (5 percent uncalcined clay, remainder control batch). These samples demonstrate the variations in product characteristics that can be expected. These samples are within the invention and are deemed suitable for use as intermediate strength proppants. These samples also exhibit lower apparent specific gravities than control samples 1 and 8-9.

Sample Nos. 11-25 were prepared from using different amounts and sources of uncalcined clay. Each of these samples is deemed suitable for use as proppants.

Generally speaking, as the amount of uncalcined clay is increased, the apparent specific gravity of the resulting pellets is reduced and effective sintering may be done at a lower temperature. Sample No. 26 is deemed marginally suitable due to its high level of fines generated on API Crush.

A comparison of the test results for Samples Nos. 1 and 5 indicates that substitution of 10 percent dust collector fines for calcined bauxite when the remaining ingredient is clay actually improves characteristics of the pellets that are considered significant for proppants. Note that Sample 5 exhibited lower apparent specific gravity, lower percent fines generated on API Crush and greater permeability than Sample No. 1. The permeability of Sample Nos. 1 and 5 was comparable. This is surprising. It was previously thought that the use of a higher amount of silica and material having a high LOI (due to substitution of dust collector fines for calcined bauxite) would result in a lower performance product due to the lower amount of alumina and greater amount of closed porosity as evidenced by lower apparent specific gravity. It was thought that use of a material having a high LOI (eg. greater than 1-2 percent) would damage the structure as the chemically bound water and volatiles are driven off during furnacing of the pellets.

Referring now to Sample Nos. 8 and 9 of Table III, it can be seen that sintering temperature has a significant effect on the strength of pellets of a given composition. For Sample Nos. 8 and 9 furnacing the dried pellets at 1495° C. provided greatest resistance to crushing as evidenced by lowest percent lines generated for API Crush and greatest amount of applied load to induce a specified compression. A value of 24+ or lack of an entry following a 24+ entry indicates that the capacity of the press was reached or would have been exceeded for the specified amount of compression.

A comparison of the results given in Table III for Sample Nos. 1 and 25 reveals that use of 60 percent uncalcined clay permits furnacing at lower temperature while yielding a product of lower apparent specific gravity, lower API Crush and greater permeability.

The composite, spherical, sintered pellets of the present invention are useful as a propping agent in methods of fracturing subterranean formations to increase the permeability thereof, particularly those formations having a compaction pressure of at least 280 kg/cm^2 (4000 psi), which are typically located at a depth 6,000 feet or greater. Pellets according to the present invention are presently believed to be particularly suitable for use at depths greater than 7,000 feet but less than 14,000 feet.

When used as a propping agent, the pellets of the present invention may be handled in the same manner as other propping agents. The pellets may be delivered to the well site in bags or in bulk form along with the other materials used in fracturing treatment. Conventional equipment and techniques may be used to place the spherical pellets as propping agent.

A viscous fluid, frequently referred to as "pad", is injected into the well at a rate and pressure to initiate and propagate a fracture in the subterranean formation. The fracturing fluid may be an oil base, water base, acid, emulsion, foam, or any other fluid. Injection of the fracturing fluid is continued until a fracture of sufficient geometry is obtained to permit placement of the propping pellets. Thereafter, pellets as hereinbefore described are placed in the fracture by injecting into the fracture a fluid into which the pellets have previously been introduced and suspended. The propping distribution is usually, but not necessarily, a multi-layer pack. The overall particle size of the pellets is between about 0.1 and about 2.5 millimeters and, more preferably, between about 0.15 and about 1.7 millimeters. Following placement of the pellets, the well is shut-in for a time sufficient to permit the pressure in the fracture to bleed off into the formation. This causes the fracture to close and apply pressure on the propping pellets which resist further closure of the fracture.

The foregoing description and embodiments are intended to illustrate the invention without limiting it thereby. It will be understood that various modifications can be made in the invention without departing from the spirit or scope thereof.

We claim:

1. A composite, sintered, spherical pellet suitable for gas and oil well proppant which is prepared from materials consisting essentially of clay materials, bauxitic

materials and alumina, wherein said materials include at least one uncalcined or partially calcined ingredient selected from the group consisting of clay materials, bauxitic materials and dust collector fines produced during the calcination of clay materials and bauxitic materials, and alumina, said pellet having on a dry weight basis an alumina-to-silica ratio from about 9:1 to about 1:1 and at least about 6.51 percent by weight of other than alumina and silica, said pellet having an apparent specific gravity of less than 3.30.

2. The pellet of claim 1 wherein a plurality of said pellets has a permeability to distilled water at about 75° F. (24° C.) which decreases not more than about three-fourths when the pressure applied to said pellets is increased from 2000 to 10,000 psi (140–700 kg/cm^2).

3. The pellet of claim 1, wherein the pellet has an alumina-to-silica dry weight basis ration from about 4:1 to about 6.5:1.

4. The pellet of claim 1, wherein the pellet has an alumina-to-silica ratio of about 5:1.

5. The pellet of claim 1, 2 or 3 wherein said pellet is of an overall size ranging from about 0.1 to 2.5 millimeters and an apparent specific gravity from about 2.6 to 3.3.

6. The pellet of claim 1, wherein the pellet is at least 85 percent by weight of Al_2O_3 and SiO_2.

7. The pellet of claim 1, wherein the pellet is not more than about 82 percent by weight of Al_2O_3.

8. The pellet of claim 1 wherein the pellet is prepared from a mixture containing on a dry weight basis from about 20 to about 40 percent calcined bauxite, from about 4 to about 10 percent dust collector fines with the remainder being calcined clay.

9. The pellet of claim 1 wherein the pellet is prepared from a mixture containing on a dry weight basis from about 5 to about 30 percent uncalcined clay with the remainder being calcined bauxite and calcined clay.

10. The pellet of claim 1 wherein the pellet is prepared from a mixture containing on a dry weight basis from about 40 to about 70 percent uncalcined clay with the remainder being calcined bauxite.

11. A sintered, spherical composite pellet suitable for use as gas and oil well proppant, said pellet having an Al_2O_3/SiO_2 dry weight basis ratio from about 9:1 to about 1:1, said pellet having an apparent specific gravity of less than 3.30 g/cc and at least about 6.51 percent by weight of other than Al_2O_3 and SiO_2, said pellet being made by a process including the steps of:

(a) Forming a particulate mixture from materials consisting essentially of clay materials, bauxitic materials and alumina wherein said materials include at least one uncalcined or partially calcined ingredient selected from the group consisting of clay materials, bauxitic materials and dust collector fines produced during the calcination of clay materials and bauxitic materials and alumina, having an average particle size of less than 15 microns in a high intensity mixture and at least about 6.51 percent on a dry weight basis other than Al_2O_3 and SiO_2;

(b) while stirring the mixture, adding sufficient water to cause formation of composite spherical pellets from the mixture;

(c) drying the pellets until less than three (3) weight percent free moisture remains in the pellets;

(d) furnacing the dried pellets at a furnace temperature ranging from about 1300° C. to about 1500° C. for a period sufficient to enable recovery of sintered, spherical, composite pellets having a bulk density from about 1.35 to 1.8 grams per cubic centimeter.

12. The pellet of claim 11, wherein the mixture is intensively stirred during step (b).

13. The pellet of claim 11, wherein the particulate mixture has an average particle size of less than about 10 microns.

14. The pellet of claim 11, further comprising, prior to step (c), adding from about 5 to about 15 percent by weight of pellets of any of the ingredients of the mixture of step (a).

15. The pellet of claim 11 wherein the dried pellets are furnaced for a period from about 4 to about 8 minutes.

16. The pellet of claim 15 wherein prior to step (c) there is added from about 5 to 15 percent by weight of pellets of the mixture of step (a) while continuing to stir the pellets.

17. A plurality of pellets as described in claim 1, having a bulk density of between about 1.35 and 1.80 grams per cubic centimeter wherein said pellets are of a diameter from about 0.1 to about 2.5 millimeters.

18. A process for manufacturing composite, sintered, spherical pellets suitable for use as gas and oil well proppant having an alumina-to-silica ratio on a dry-weight-basis from about 9:1 to about 1:1 and at least about 6.51 percent by weight of other than alumina and silica, said process comprising the steps of:

(a) adding to a high-intensity mixer, in predetermined ratio, starting ingredients consisting essentially of clay materials, bauxitic materials and alumina wherein said materials include at least one uncalcined or partially calcined ingredient selected from the group consisting of clay materials, bauxite materials and dust collector fines produced during the calcination of clay materials and bauxitic materials, to materials consisting essentially of calcined clay materials and/or a member of the group of calcined bauxite materials, alumina or mixtures thereof, each ingredient having an average particle size of less than 15 microns;

(b) stirring said starting ingredients to form a particulate mixture having an average particle size of less than 15 microns and at least about 6.51 percent on a dry weight basis of other than alumina and silica;

(c) while stirring the mixture, adding sufficient water to cause formation of composite, spherical pellets from the mixture;

(d) drying the pellets until less than ten (10) weight percent free moisture remains in the pellets;

(e) furnacing the dried pellets at a furnace temperature of from about 1300° C. to about 1500° C. for a period sufficient to enable recovery of sintered, spherical, composite pellets having a bulk density of from about 1.35 to about 1.80 grams per cubic centimeter and at least about 6.51 percent by weight of other than alumina and silica.

19. The process of claim 18 wherein the pellets are dried at a temperature between about 100° C. and about 300° C. until less than three (3) weight percent free moisture remains in the pellets.

20. The process of claim 18 wherein each ingredient of the particulate mixture has an average particle size of less than 10 microns.

21. The process of claim 18, further comprising, prior to step (d), adding from about 5 to about 15 percent of any of the ingredients given in step (a).

22. The process of claim 18, wherein the dried pellets are furnaced for a period from about 4 to about 20 minutes.

23. The process of claim 18, further comprising, prior to step (d), adding from about 5 to 15 percent of any of the ingredients given in step (a) while stirring the pellets.

24. A gas and oil well proppant comprising a plurality of composite, sintered, spherical pellets having a permeability to distilled water at about 75° F. (24° C.) which decreases not more than about three-fourths when the pressure applied to said pellets is increased from 2000 to 10,000 psi (140–700 kg/cm^2), said pellets being prepared from, on a dry weight basis, materials consisting essentially of clay materials, bauxitic materials and alumina wherein said materials include at least one uncalcined or partially calcined ingredient selected from the group consisting of clay materials, bauxitic materials and dust collector fines produced during calcination of clay materials and bauxitic materials, and alumina, or mixtures thereof, said pellets having an alumina-to-silica dry weight basis ratio from about 9:1 to about 1:1, said pellets having an apparent specific gravity of less than 3.30 and at least about 6.51 weight percent of other than alumina and silica and a diameter between about 0.1 and about 2.5 millimeters.

25. The pellet of claim 1 wherein said pellet is prepared from a mixture consisting essentially of clay materials and bauxitic materials.

26. The method of claim 18 wherein fluxes are not added to the high-intensity mixer.

* * * * *

EXHIBIT 8

```
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Originator-Name: webmaster@www.sec.gov
Originator-Key-Asymmetric:
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CONFORMED SUBMISSION TYPE:      10-K
PUBLIC DOCUMENT COUNT:          5
CONFORMED PERIOD OF REPORT:     19971231
FILED AS OF DATE:               19980316
SROS:                   NASD

FILER:

        COMPANY DATA:
                COMPANY CONFORMED NAME:                 CARBO CERAMICS INC
                CENTRAL INDEX KEY:                      0001009672
                STANDARD INDUSTRIAL CLASSIFICATION:     ABRASIVE ASBESTOS & MISC NONMETALLIC MINERAL PRODUCTS [3290]
                IRS NUMBER:                             721100013
                STATE OF INCORPORATION:                 DE
                FISCAL YEAR END:                        1231

        FILING VALUES:
                FORM TYPE:              10-K
                SEC ACT:
                SEC FILE NUMBER:        000-28178
                FILM NUMBER:            98566228

        BUSINESS ADDRESS:
                STREET 1:               600 EAST LAS COLINAS BLVD
                STREET 2:               STE 1520
                CITY:                   IRVING
                STATE:                  TX
                ZIP:                    75039
                BUSINESS PHONE:         2144010090

        MAIL ADDRESS:
                STREET 1:               600 E LAS COLINAS BLVD
                STREET 2:               STE 1520
                CITY:                   IRVING
                STATE:                  TX
                ZIP:                    75039
</SEC-HEADER>
<DOCUMENT>
<TYPE>10-K
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<DESCRIPTION>FORM 10-K FOR YEAR ENDED DECEMBER 31, 1997
<TEXT>

<PAGE>   1

================================================================================

                       SECURITIES AND EXCHANGE COMMISSION
                             Washington, D.C. 20549

                                   FORM 10-K

    [X] ANNUAL REPORT PURSUANT TO SECTION 13 OR 15(d) OF THE SECURITIES EXCHANGE
        ACT OF 1934 FOR THE FISCAL YEAR ENDED DECEMBER 31, 1997.

    [ ] TRANSITION REPORT PURSUANT TO SECTION 13 OR 15(d) OF THE SECURITIES
        EXCHANGE ACT OF 1934.

                           COMMISSION FILE NO. 0-28178

                               CARBO CERAMICS INC.

                 (Exact name of registrant as specified in its charter)

<TABLE>
<S>                                                <C>
                DELAWARE                                          72-1100013
     (State or other jurisdiction of                          (I.R.S. Employer
      incorporation or organization)                        Identification Number)
</TABLE>
```

600 E. LAS COLINAS BOULEVARD
SUITE 1520
IRVING, TEXAS 75039
(Address of principal executive offices)

(972) 401-0090
(Registrant's telephone number)

Securities registered pursuant to Section 12(b) of the Act: NONE

Securities registered pursuant to Section 12(g) of the Act:
COMMON STOCK, PAR VALUE $0.01 PER SHARE

Indicate by check mark whether the registrant (1) has filed all reports required to be filed by Section 13 or 15(d) of the Securities Exchange Act of 1934 during the preceding 12 months (or for such shorter period that the registrant was required to file such reports), and (2) has been subject to such filing requirements for the past 90 days. Yes [X] No [ ]

Indicate by check mark if disclosure of delinquent filers pursuant to Item 405 of Regulation S-K is not contained herein, and will not be contained, to the best of registrant's knowledge, in definitive proxy or information statements incorporated by reference in Part III of this Form 10-K or any amendment to this Form 10-K. [ ]

The aggregate market value of the voting stock held by non-affiliates of the Registrant, based upon the closing sale price of the Common Stock on March 6, 1998, as reported on the Nasdaq National Market, was approximately $105,937,000. Shares of Common Stock held by each officer and director and by each person who owns 5% or more of the outstanding Common Stock have been excluded in that such persons may be deemed to be affiliates. This determination of affiliate status is not necessarily a conclusive determination for other purposes.

As of March 6, 1998, Registrant had outstanding 14,602,000 shares of Common Stock.

DOCUMENTS INCORPORATED BY REFERENCE

Portions of the Proxy Statement for Registrant's Annual Meeting of Shareholders to be held April 14, 1998 are incorporated by reference in Part III.

==

PART I

ITEM 1. BUSINESS

GENERAL

CARBO Ceramics Inc. is the world's largest producer and supplier of ceramic proppants for use in the hydraulic fracturing of natural gas and oil wells. Demand for ceramic proppants depends generally upon the demand for natural gas and oil and on the number of natural gas and oil wells drilled, completed or recompleted worldwide. More specifically, the demand for ceramic proppants is dependent on the number of oil and gas wells that are hydraulically fractured to stimulate production.

The hydraulic fracturing process consists of pumping fluids down a natural gas or oil well at pressures and flow rates sufficient to split the hydrocarbon bearing formation and create fractures in the formation. A granular material, such as ceramic proppant or sand-based proppant, is suspended in the fluid and packs the newly created fracture, keeping the fracture open once high-pressure pumping stops. The proppant-filled fracture creates a permeable channel through which the hydrocarbons can flow more freely from the formation to the well and then to the surface.

CARBO Ceramics was formed in 1987 for the purpose of purchasing the assets of Standard Oil Proppants Company Ltd. (SOPCO). SOPCO was a joint venture formed to operate the combined proppant businesses of the Carborundum Company and Dresser Industries. These proppants businesses were started in 1978 and 1984 respectively. While the Carborundum Company and Dresser Industries had primarily manufactured high strength, premium priced proppants for use in very deep wells, CARBO Ceramics has pursued a strategy of introducing new, lower-priced, lightweight, intermediate strength ceramic proppants to capture a greater portion of the large market for sand-based proppants.

The Company estimates that it supplies 60% of the ceramic proppants and 5% of all proppants used worldwide.

PRODUCTS

The Company's four product lines cover the entire spectrum of commercially available ceramic proppants. CARBOHSP(TM) and CARBOPROP(R) are premium priced, high strength proppants designed primarily for use in deep gas wells. CARBOHSP(TM), which was introduced in 1979, is the original ceramic proppant, formerly marketed as "Sintered Bauxite". CARBOHSP(TM) offers the highest level of strength and conductivity for use primarily in deep gas wells. CARBOPROP(R), which was introduced by the Company in 1982, is slightly lower in weight and strength than CARBOHSP(TM) and was developed for use in deep gas wells that do not require the strength of CARBOHSP(TM).

The CARBOLITE(R) and CARBOECONOPROP(R) products are lightweight, intermediate strength proppants designed for use in gas wells of moderate depth and shallower oil wells. The products are manufactured and sold to compete directly with sand-based proppants. CARBOLITE(R), introduced in 1984, is used in medium depth oil and gas wells, where the additional strength of ceramic proppants may not be essential, but where higher production rates can be achieved due to the products' roundness and uniform grain size.

CARBOECONOPROP(R), introduced in 1992 to compete directly with sand-based proppants, is the Company's lowest priced and fastest growing product. The introduction of CARBOECONOPROP(R) has resulted in ceramics being used in many new markets by end users that had not previously used ceramic proppants. The Company believes that many of the users of CARBOECONOPROP(R) had previously used sand or resin-coated sand. The Company further believes that its ability to continue to penetrate the market for sand-based proppants in 1997 was limited by its production capacity for lightweight ceramic proppants.

CUSTOMERS AND MARKETING

The Company's largest customers are, in alphabetical order, BJ Services Company, Dowell and Halliburton Company, the three largest participants in the worldwide petroleum pressure pumping industry.

These companies collectively accounted for approximately 84% of the Company's 1997 revenues. The Company's other customers include primarily foreign pumping service companies, that compete in the worldwide fracturing business. The end users of the Company's products, however, are the operators of natural gas and oil wells that engage pumping service companies to hydraulically fracture wells to improve the recovery of natural gas or oil wells, thereby enhancing the rate of return on the investment made in such wells. The Company works with the pressure pumping service companies to present the advantages of using ceramic proppants to the operators of natural gas and oil wells. The Company generally supplies its customers with products on a just-in-time basis, with transactions governed by individual purchase orders. Continuing sales of product depend on the Company's direct customers and the well operators being satisfied with both product and delivery performance.

The Company recognizes the importance of aggressive marketing when introducing a technically advanced and performance enhancing, but intrinsically more costly, product. The Company must market its products both to its direct customers and to owners and operators of the natural gas and oil wells. The Company's sales and marketing staff regularly calls on and keeps close contact with the people who are influential in the proppant purchasing decision: production companies, regional offices of well service companies that offer pressure pumping services, and various completion engineering consultants. The Company provides a variety of technical support services and has developed computer software that models the return on investment achievable by using the Company's ceramic proppants versus that of other proppants in the hydraulic fracturing of a natural gas or oil well.

The Company's Vice President of Marketing and Technology coordinates worldwide sales and marketing activities. The Company's export marketing efforts are conducted through its sales office in Aberdeen, Scotland and through two commissioned sales agents located in South America and Australia.

The Company's ceramic proppants are used worldwide by U.S. customers operating abroad and by foreign customers. Sales outside the United States accounted for 37%, 31% and 37% of the Company's sales for 1995, 1996 and 1997, respectively.

The distribution of the Company's export and domestic revenues is shown below, based upon the region in which proppants were used by the customer:

<TABLE>
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	1995	1996	1997
	($ IN MILLIONS)		

<S>	<C>	<C>	<C>
LOCATION			
United States	$36.8	$45.3	$53.3
International	21.2	19.9	31.8
Total	$58.0	$65.2	$85.1

</TABLE>

COMPETITION AND MARKET SHARE

The Company's chief worldwide competitor is Norton-Alcoa Proppants ("Norton-Alcoa"). Norton-Alcoa is a joint venture of Compagnie de Saint-Gobain, a French glass and materials company, and Aluminum Company of America. Norton-Alcoa manufactures ceramic proppants that directly compete with each of the Company's products. In addition, Mineraco Curimbaba ("Curimbaba"), based in Brazil, manufactures a sintered bauxite product similar to the Company's CARBOHSP(TM), which is marketed in the United States under the name "Sinterball". The Company believes that Curimbaba has not expanded its U.S. product line to include a full range of ceramic proppants and is unlikely to do so in light of patents held by the Company and Norton-Alcoa. The Company believes that it supplies approximately 60% of the ceramic proppants and approximately 5% of all proppants used by the oilfield services companies that perform fracturing services worldwide.

Competition for CARBOHSP(TM) and CARBOPROP(R) includes ceramic proppants manufactured by Norton-Alcoa and Curimbaba. The Company's CARBOLITE(R) and CARBOECONOPROP(R) products compete with ceramic proppants produced by Norton-Alcoa and with sand-based proppants for use in the hydraulic fracturing of medium depth natural gas and oil wells. The leading suppliers of mined sand are

Unimin Corp., Badger Mining Corp., Wedron Silica Co., Ogelbay-Norton Company and Colorado Silica Sand, Inc. The leading suppliers of resin-coated sand are Borden Proppants Corp. and Santrol, a subsidiary of Fairmont Minerals Limited, Inc.

The Company believes that the most significant factors that influence a customer's decision to purchase the Company's products are: (i) price/performance ratio, (ii) on-time delivery performance, (iii) technical support and (iv) proppant availability. The Company believes that its products are competitively priced and that its delivery performance is excellent. The Company also believes that its superior technical support has enabled it to persuade customers to use ceramic proppants in an increasingly broad range of applications and thus increased the overall market for the Company's products.

Prior to 1997, the Company had generally maintained sufficient inventory to satisfy demand for its products. However, in 1997, it became obvious to the management of the Company that previous capacity additions were insufficient to satisfy demand in an improving market. The Company has addressed this issue through the construction of a new manufacturing facility in McIntyre, Georgia which is scheduled for completion in the fourth quarter of 1998.

The Company continually conducts testing and development activities with respect to alternative raw materials to be used in the Company's existing production methods and alternative production methods. The Company is not aware of the development of alternative products for use as proppants in the hydraulic fracturing process. The Company believes that the main barriers to entry for additional competitors are the patent rights held by the Company and certain of its current competitors and the capital costs involved in building production facilities of sufficient size to be operated efficiently.

DISTRIBUTION

The Company maintains finished goods inventories at its plants in New Iberia, Louisiana, and Eufaula, Alabama, and at six remote stocking facilities located in: Rock Springs, Wyoming; Oklahoma City, Oklahoma; San Antonio, Texas; Fairbanks, Alaska; Edmonton, Alberta, Canada; and Rotterdam, The Netherlands. The remote stocking facilities consist of bulk storage silos with truck trailer loading facilities. The Company owns the facilities in San Antonio, Rock Springs and Edmonton and subcontracts the operation of the facilities and transportation to a local trucking company. The remaining stocking facilities are owned and operated by local trucking companies under contract with the Company. The North American sites are supplied by rail, and the site in the Netherlands is supplied by container ship. In total, the Company leases 79 rails cars, and owns or leases 62 dedicated trailers. The price of the Company's products sold for delivery in the lower 48 United States and Canada includes just-in-time delivery of proppants to the operator's well site, which eliminates the need for customers to maintain an inventory of ceramic proppants.

The Company increased storage capacity at its remote storage facilities in San Antonio, Rock Springs and Edmonton in 1997 at a cost of approximately $4.1

million.

RAW MATERIALS

Ceramic proppants are made from alumina-bearing ores (commonly referred to as bauxite, bauxitic clay or kaolin, depending on the alumina content), which are readily available on the world market. Bauxite is largely used in the production of aluminum metal, refractory material and abrasives. The main deposits of alumina-bearing ores in the United States are in Arkansas, Alabama and Georgia; other economically mineable deposits are located in Australia, China, Jamaica, Russia and Surinam.

The Company's New Iberia facility currently uses bauxite imported from Australia and bauxitic clay mined in Arkansas. The Company has decreased its dependence on imported bauxite and bauxitic clay as it has entered into a long-term contract for the processing and supply of Arkansas bauxite and bauxitic clay for use at the New Iberia facility. The Company believes that this agreement, which stipulates a fixed price, subject to annual upward adjustments in accordance with a producer price index, will provide a sufficient supply of bauxite and bauxitic clay to meet the requirements of the New Iberia facility through 1999.

The Company's Eufaula facility exclusively employs locally mined uncalcined kaolin, and the Company has entered into a contract requiring the supplier to sell to the Company up to 200,000 net tons of kaolin per year and the Company to purchase from the supplier 80% of the Eufaula facility's annual kaolin requirements, each through 2003. This agreement stipulates a fixed price, subject to annual adjustment in accordance with fluctuations (within an 8% annual limit) in the producer price index. Raw material costs for the Eufaula facility are substantially below those for the New Iberia plant, due to the Eufaula facility's proximity to raw material reserves and use of uncalcined raw materials.

The new production facility in McIntyre, Georgia will also utilize primarily locally mined uncalcined kaolin. The Company has entered into a long-term supply agreement for these raw materials which stipulates a fixed price subject to annual adjustments for changes in the producer price index and fuel costs. The supply contract provides for a twenty-year supply of raw materials.

PRODUCTION PROCESS

Ceramic proppants are made by grinding or dispersing ore to a fine powder, combining the powder into small, green (i.e., unfired) pellets and sintering the pellets at 2,500F to 3,000F in a rotary kiln.

The Company uses two different methods to produce ceramic proppants. The Company's plant in New Iberia, Louisiana, uses a dry process (the "Dry Process") which starts with bauxite or bauxitic clay which has been dried to remove both free water and water which was chemically bound within the ore. This drying process is referred to as calcining. The calcined ores are received at the plant and ground into a dry powder. Pellets are formed by combining the powder with water and binders and introducing the mixture into a high-shear mixer. The process is completed once the green pellets are sintered in a rotary kiln. The Company's competitors also use the Dry Process to produce ceramic proppants.

The Company's plant in Eufaula, Alabama, uses a wet process (the "Wet Process"), which starts with moist, uncalcined kaolin from local mines. The kaolin is dispersed with chemicals in a water slurry. With an atomizer, the slurry is sprayed like a mist into a dryer which causes the slurry to harden into green pellets. Finally, these green pellets are sintered in rotary kilns. The Company believes that the Wet Process is unique to its plant in Eufaula, Alabama.

The Company's plant in McIntrye, Georgia will use the Dry Process. However, the Company expects to maintain lower production costs at this facility by purchasing locally mined ore and performing the calcining process itself.

PATENT PROTECTION

The Company's ceramic proppants are made by processes and techniques that involve a high degree of proprietary technology, some of which is protected by patents.

The Company owns outright six issued U.S. patents and seven issued foreign patents; three of these U.S. patents and four of these foreign patents relate to the CARBOPROP(R) product produced by the Dry Process.

The Company jointly owns with A/S NIRO Atomizer ("NIRO"), the Danish designer and manufacturer of the spray atomizer device used in the Wet Process, three issued U.S. patents and 17 issued foreign patents. The patents owned jointly with NIRO generally relate to the Wet Process, and the products produced thereby (CARBOLITE(R) and CARBOECONOPROP(R)).

The current versions of the Company's six most important U.S. patents expire at various times in the years 2002 through 2009 with its two key product patents expiring in 2006 and 2009. The Company believes that these patents have been and will continue to be important in enabling the Company to compete in the market to supply proppants to the natural gas and oil industry. The Company intends to enforce and has in the past vigorously enforced its patents. The Company may be involved from time to time in the future, as it has been in the past, in litigation to determine the enforceability, scope and validity of its patent rights. Past disputes with its main competitor have been resolved in ways that permit the Company to continue to benefit fully from its patent rights. The Company and this competitor have cross-licensed certain of their respective

patents relating to intermediate and low density proppants on both a royalty-free and royalty-bearing basis. (Royalties under these licenses are not material to the Company's financial results.) The Company and NIRO have not granted any licenses to third parties relating to the use of the Wet Process. As a result of these cross licensing arrangements, both the Company and its main competitor are able to produce a broad range of ceramic proppants, while third parties are unlikely to be able to enter the ceramic proppants market without infringing on the patent rights held by the Company, its main competitor or both.

PRODUCTION CAPACITY

The Company believes that constructing adequate capacity ahead of demand while incorporating new technology to reduce manufacturing costs are important competitive strategies to increase its overall share of the market for proppants. Prior to 1993, the Company's production capacity was substantially in excess of its sales requirements. Since that time, however, the Company has been expanding its capacity in order to meet the generally increasing demand for its products. In October 1993, the Company increased the capacity of the Eufaula facility from 90 million pounds per year to 170 million pounds per year, in response to the increasing demand for the Company's CARBOLITE(R) and CARBOECONOPROP(R) products. In May 1995, the Company completed a 40 million pound per year capacity expansion at the New Iberia facility, intended to meet increasing demand for CARBOHSP(TM) and CARBOPROP(R). Most recently, in February 1996, the Company commenced operations of its second 80 million pound per year expansion of the Eufaula plant. Total annual capacity is currently 100 million pounds at the New Iberia facility and is 250 million pounds at the Eufaula facility.

In July 1997, the Company began construction of a new $40 million manufacturing facility in McIntyre, Georgia. The plant is expected to be completed in the fourth quarter of 1998 and is expected to have initial capacity of 200 million pounds per year. The plant will be capable of producing all of the Company's product lines and has been designed to be expandable to a capacity of 400 million pounds per year.

The following table sets forth the date of construction of and recent expansion of the Company's manufacturing facilities:

<TABLE>
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LOCATION	YEAR OF COMPLETION	ANNUAL CAPACITY (MILLIONS OF POUNDS)	PRODUCTS
<S>	<C>	<C>	<C>
New Iberia, Louisiana			
Unit 1.............	1979	20	CARBOHSP(TM) and CARBOPROP(R)
Unit 2.............	1981	40	CARBOHSP(TM) and CARBOPROP(R)
1995 Expansion.....	1995	40	CARBOHSP(TM) and CARBOPROP(R)
Total......		100	
Eufaula, Alabama			
Unit 3.............	1983	90	CARBOLITE(R) and CARBOECONOPROP(R)
1993 Expansion.....	1993	80	CARBOLITE(R) and CARBOECONOPROP(R)
1996 Expansion.....	1996	80	CARBOLITE(R) and CARBOECONOPROP(R)
Total......		250	

		===	
McIntyre, Georgia(1) Units 1 and 2......	1998	200	CARBOLITE(R), CARBOECONOPROP(R) CARBOHSP(TM) and CARBOPROP(R)

</TABLE>

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(1) The McIntyre, Georgia plant is expected to be completed in the fourth quarter of 1998, and is expected to have an initial installed capacity of 200 million pounds per year.

ORDER BACKLOG

The Company generally operates without any material backlog.

ENVIRONMENTAL AND OTHER GOVERNMENTAL REGULATIONS

The Company believes that its operations are in substantial compliance with applicable federal, state and local environmental and safety laws and regulations. The Company does not anticipate any significant expenditures in order to continue to comply with such laws and regulations.

EMPLOYEES

At December 31, 1997, the Company had 117 full-time employees. In addition to the services of its employees, the Company employs the services of consultants as required. The Company's employees are not represented by labor unions. There have been no work stoppages or strikes during the last three years that have resulted in the loss of production or production delays. The Company believes its relations with its employees are satisfactory.

FORWARD-LOOKING INFORMATION

The Private Securities Litigation Reform Act of 1995 provides a "safe harbor" for forward-looking statements. This Form 10-K, the Company's Annual Report to Shareholders, any Form 10-Q or any Form 8-K of the Company or any other written or oral statements made by or on behalf of the Company may include forward-looking statements which reflect the Company's current views with respect to future events and financial performance. These forward-looking statements are subject to certain risks and uncertainties that could cause actual results to differ materially from such statements. This document contains forward-looking statements within the meaning of the Private Securities Litigation Reform Act of 1995 concerning, among other things, the Company's prospects, developments and business strategies for its operations, all of which are subject to certain risks, uncertainties and assumptions. These risks and uncertainties include but are not limited to, changes in the demand for oil and natural gas, the development of alternative stimulation techniques and the development of alternative proppants for use in hydraulic fracturing. The words "believe", "expect", "anticipate", "project" and similar expressions identify forward-looking statements. Readers are cautioned not to place undue reliance on these forward-looking statements, which speak only as of the date the statement was made. The Company undertakes no obligation to publicly update or revise any forward-looking statements, whether as a result of new information, future events or otherwise.

ITEM 2. PROPERTIES

The Company maintains its corporate headquarters (approximately 2,700 square feet of leased office space) in Irving, Texas, and owns its manufacturing facilities, land and substantially all of the related production equipment in New Iberia, Louisiana, and Eufaula, Alabama.

The facility in New Iberia, Louisiana, located on 24 acres of land owned by the Company, consists of two production units (approximately 85,000 square feet), a laboratory (approximately 4,000 square feet) and an office building (approximately 3,000 square feet). The Company also owns an 80,000 square foot warehouse on the plant grounds in New Iberia, Louisiana.

The facility in Eufaula, Alabama, located on 14 acres of land owned by the Company, consists of one production unit (approximately 111,000 square feet), a laboratory (approximately 2,000 square feet) and an office (approximately 1,700 square feet).

The Company's customer service and distribution operations are located at the New Iberia facility, while its quality control, testing and development functions operate out of both the New Iberia and Eufaula facilities. The Company owns distribution facilities in San Antonio, Texas, Rock Springs, Wyoming and Edmonton, Alberta, Canada.

EXHIBIT 10

United States Patent [19]

Lunghofer

[11] **Patent Number: 4,522,731**

[45] **Date of Patent: Jun. 11, 1985**

[54] HYDRAULIC FRACTURING PROPPING AGENT

[75] Inventor: **Eugene P. Lunghofer**, Youngstown, N.Y.

[73] Assignee: **Dresser Industries, Inc.**, Dallas, Tex.

[21] Appl. No.: **437,206**

[22] Filed: **Oct. 28, 1982**

[51] **Int. Cl.**^{3} **C09K 3/00**

[52] **U.S. Cl.** .... **252/8.55 R**; 166/280

[58] **Field of Search** .... 252/8.55 R, 8.55 B; 166/280, 307, 308; 425/6

[56] References Cited

U.S. PATENT DOCUMENTS

3,347,798	10/1967	Baer et al.	252/448
3,350,482	10/1967	Bowers	264/13
3,856,441	12/1974	Suzukawa et al.	425/7
3,976,138	8/1976	Colpoys et al.	166/280
4,053,375	10/1977	Roberts et al.	204/67
4,068,718	1/1978	Cooke et al.	166/280
4,140,773	2/1979	Stowell et al.	423/628

FOREIGN PATENT DOCUMENTS

1045027	12/1976	Canada .
137042	1/1978	Denmark .
2948584	6/1980	Fed. Rep. of Germany .
1483696	6/1967	France .
1411135	10/1975	United Kingdom .
1421531	1/1976	United Kingdom .
2037727	7/1980	United Kingdom .

OTHER PUBLICATIONS

"Hydraulic Fracturing with a High Strength Proppant" *Amer. Inst. Mining Metallurgical and Petroleum Engrs., Inc.*, Cooke, 1976.

"Light Weight Proppants for Deep Gas Well Stimulation", *Terra Tek*, Jones et al, Jun. 1980.

"The Effect of Various Proppants and Proppant Mixtures on Fracture Permeability" *SPE*, McDaniel et al., 1978.

Chem. Abstracts, vol. 85, No. 24, p. 253, 181 . . . 448a.

Primary Examiner—Benjamin R. Padgett
Assistant Examiner—T. J. Wallen
Attorney, Agent, or Firm—Finnegan, Henderson, Farabow, Garrett & Dunner

[57] **ABSTRACT**

A high strength propping agent for use in hydraulic fracturing of subterranean formations comprising solid, spherical particles having an alumina content of between 40 and 60%, a density of less than 3.0 gm/cc and an ambient temperature permeability of 100,000 or more millidarcies at 10,000 psi.

3 Claims, 5 Drawing Figures

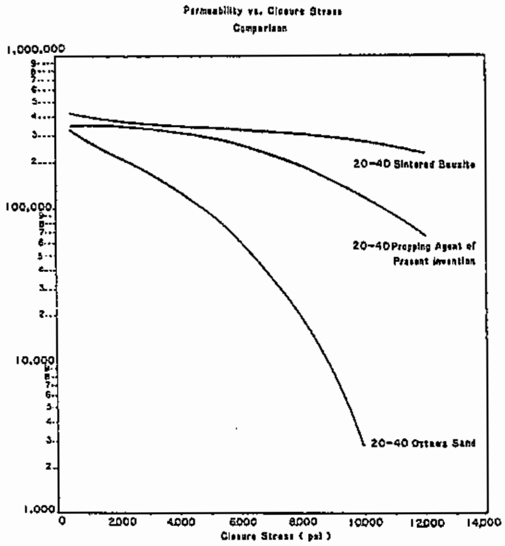
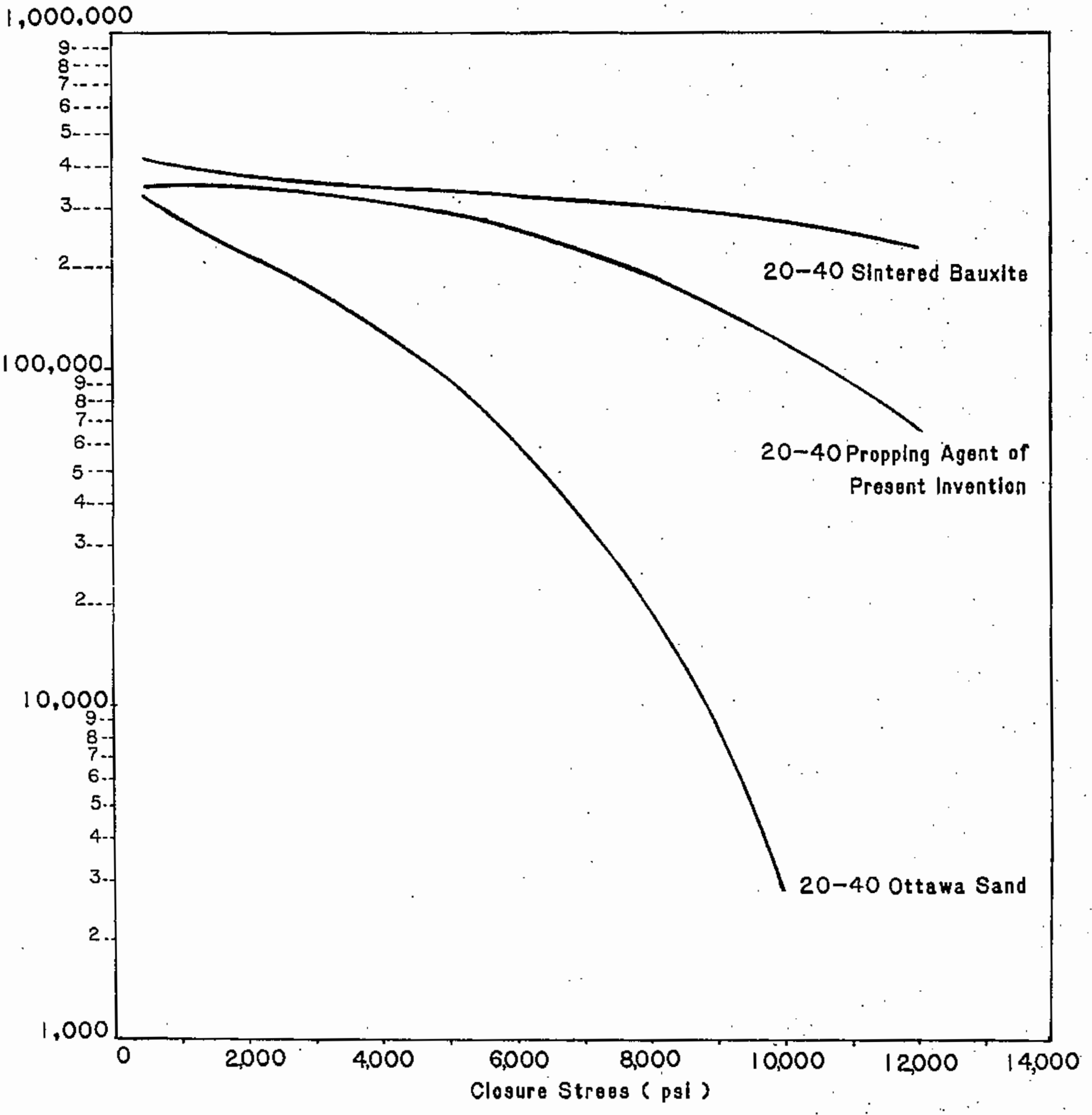


FIG. 1



Permeability vs. Closure Stress Comparison

FIG. 2

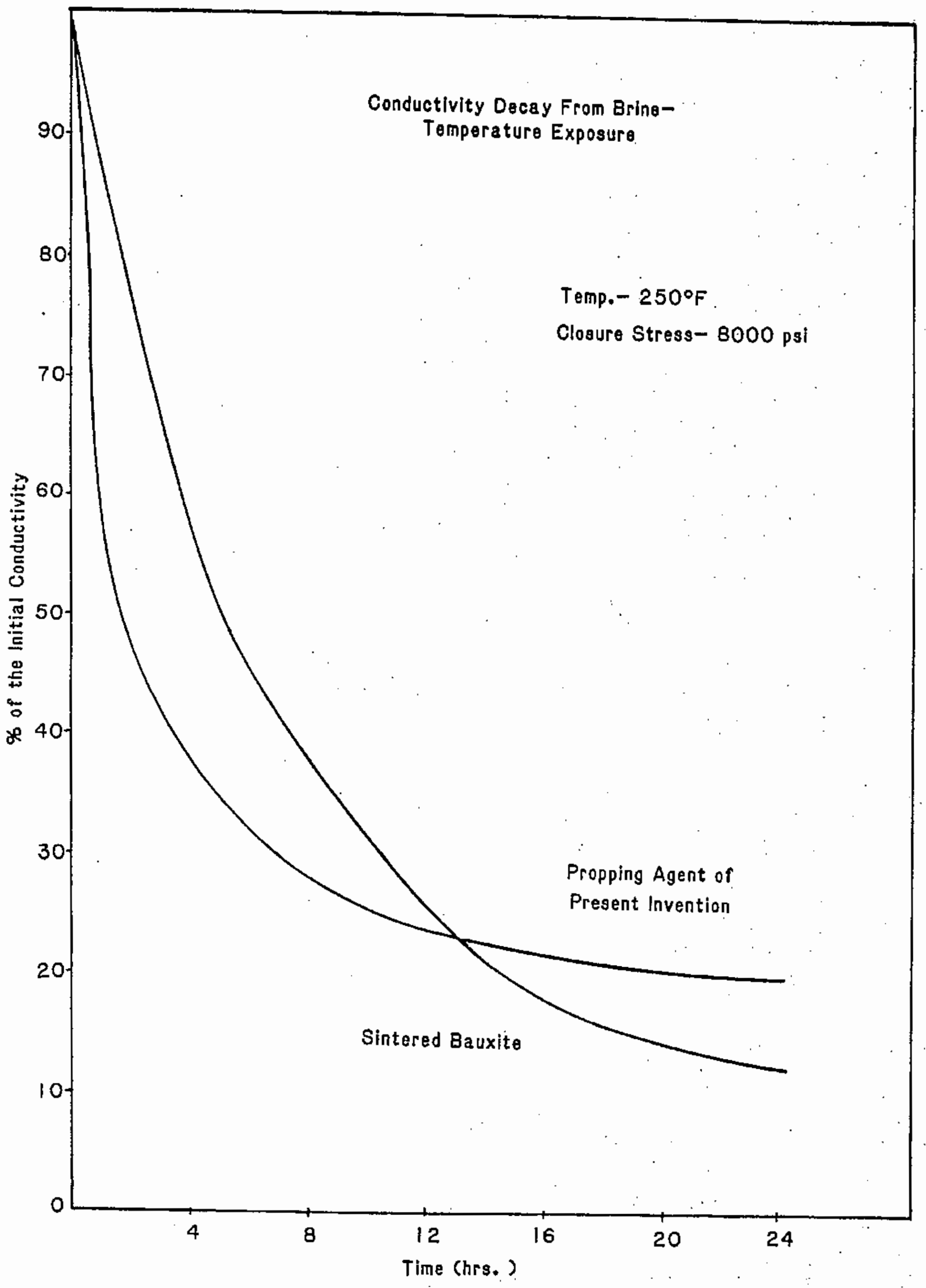

Conductivity Decay From Brine-Temperature Exposure
Temp.- 250°F
Closure Stress- 8000 psi
Propping Agent of Present Invention
Sintered Bauxite
% of the Initial Conductivity
90
80
70
60
50
40
30
20
10
0
4
8
12
16
20
24
Time (hrs.)

FIG. 3

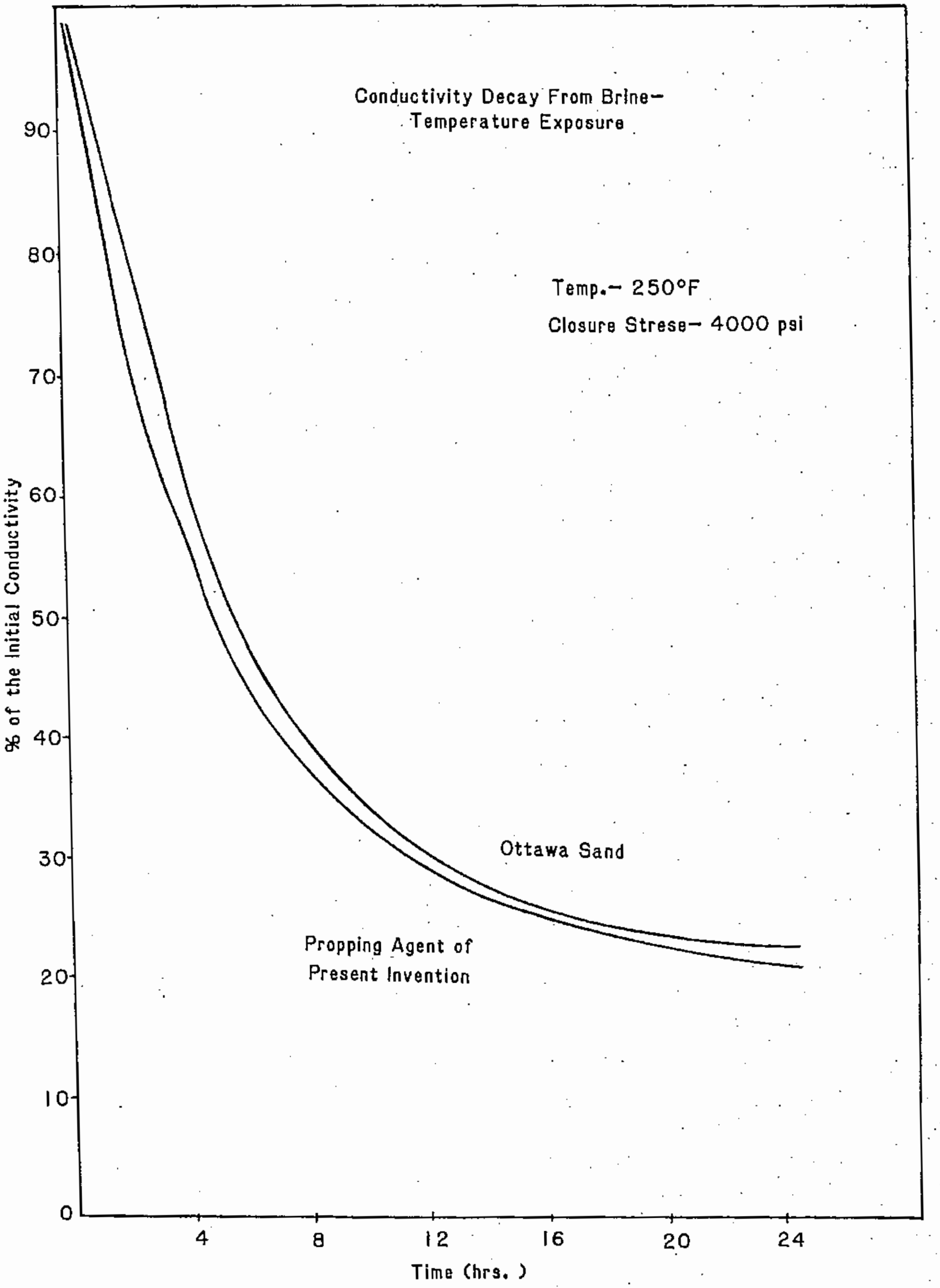

Conductivity Decay From Brine–Temperature Exposure
Temp.– 250°F
Closure Strese– 4000 psi
% of the Initial Conductivity
90
80
70
60
50
40
30
20
10
0
Ottawa Sand
Propping Agent of Present Invention
4
8
12
16
20
24
Time (hrs.)

FIG. 4

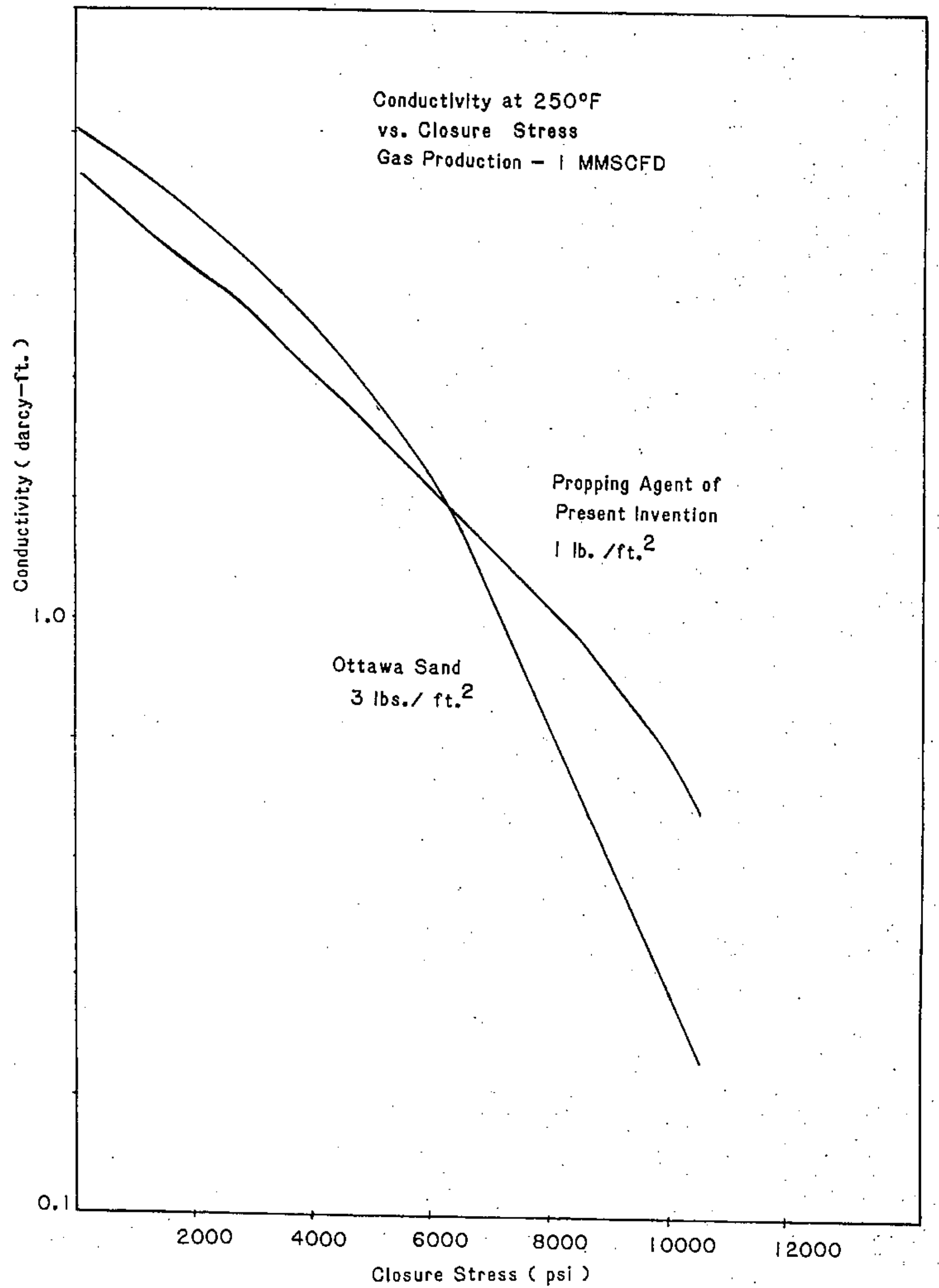
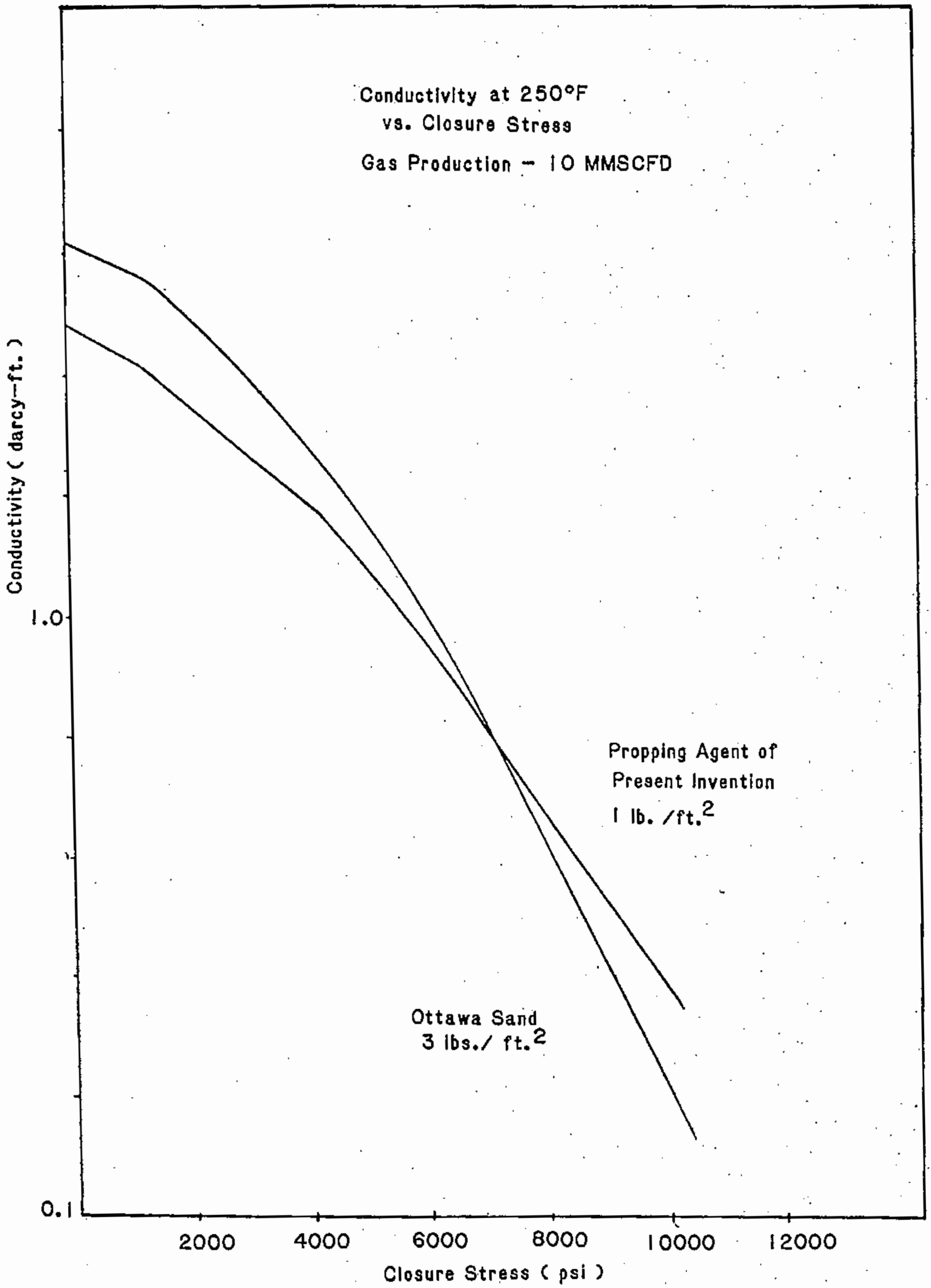

Conductivity at 250°F
vs. Closure Stress
Gas Production – 1 MMSCFD
Propping Agent of
Present Invention
1 lb. /ft.2
Ottawa Sand
3 lbs./ ft.2
Conductivity (darcy–ft.)
1.0
0.1
2000
4000
6000
8000
10000
12000
Closure Stress (psi)

FIG. 5


Conductivity at 250°F
vs. Closure Stress
Gas Production - 10 MMSCFD
Conductivity (darcy-ft.)
1.0
0.1
2000
4000
6000
8000
10000
12000
Closure Stress (psi)
Propping Agent of
Present Invention
1 lb. /ft.²
Ottawa Sand
3 lbs./ ft.²

HYDRAULIC FRACTURING PROPPING AGENT

BACKGROUND OF THE INVENTION

The present invention relates to propping agents for use in hydraulic fracturing of subterranean formations surrounding oil wells, gas wells, and similar boreholes.

Hydraulic fracturing is a well stimulation technique designed to increase the productivity of a well by creating highly conductive fractures or channels in the producing formation surrounding the well. The process normally involves two steps. First a fluid is injected into the well at a sufficient rate and pressure to rupture the formation thereby creating a crack (fracture) in the reservoir rock. Thereafter a particulate material (propping agent) is placed into the formation to "prop" open the fracture.

In order for well stimulation to occur, the propping agent must have sufficient mechanical strength to withstand the closure stresses exerted by the earth. If the propping agent is not strong enough to resist the earth's closure stresses, then the propping agent will tend to disintegrate thereby reducing the permeability of the propped fracture.

On the other hand, the propping agent must also be inexpensive since large volumes of propping agent are used in a well stimulation treatment. For example, it takes 135,520 pounds of sintered bauxite propping agent to fill a 968 ft^3 fracture. McDaniel et al., "The Effect of Various Proppants and Proppant Mixtures on Fracture Permeability," SOCIETY OF PETROLEUM ENGINEERS OF AIME, AIME Paper No. SPE 7573 (1978) at p. 4 (McDaniel et al.)

Because of its low cost, relative abundance and low density, sand is the ideal propping agent for hydraulic fracturing of low closure stress (4,000 psi or less) formations. While specially screened (usually 20–40 mesh) high grade sand (e.g., Ottawa sand) can be used with higher closure stress formations, performance drops off drastically as stress increases, particularly above 8,000 psi. At stresses of 10,000 psi and above even the highest grade sand is inadequate.

Heretofore, the only propping agents known to be able to withstand closure pressures of 10,000 psi or greater was a high density sintered bauxite propping agent. Cooke, "Hydraulic Fracturing with a High-Strength Proppant", SOCIETY OF PETROLEUM ENGINEERS OF AIME, AIME Paper No. SPE 6213 (1976); Jones et al., "Light Weight Proppants for Deep Gas Well Stimulation", submitted to Bartlesville Energy Technology Center by Terra Tek, Inc., under Government Contract # DE-AC19-79BC10038 (June 1980) (Terra Tek paper); McDaniel et al. Described in U.S. Pat. No. 4,068,718 (Cooke et al.), this high strength propping agent consists of sintered bauxite particles having a specific gravity greater than 3.4. High density is described as a critical feature of this propping agent. According to Cooke et al., the high density is necessary to attain high strength and resist fragmentation under high stress levels. They explain that permeability drops off significantly when low density particles (specific gravity below 3.4) are used. (Col. 6, lines 6–35.)

High grade alumina propping agents were also reported to be able to withstand closure pressures of 10,000 psi in U.S. Pat. No. 3,976,138 (Colpoys et al.). This, however, has not been confirmed by independent investigators. In any event, the Colpoys et al. propping agent also consists of high density particles, i.e., specific gravities of 3.40 and greater. Although Colpoys et al. describe a lower density low grade alumina propping agent as well, they do not report that this less preferred propping agent is able to withstand such severe conditions.

While the sintered bauxite propping agent is advantageous in that it can withstand closure pressures of 10,000 psi or greater, there are certain disadvantages associated with its use. On account of its high-density, it requires high viscosity fracturing fluids and/or high pumping rates along with low proppant concentration. This makes fracture control and high conductivity fractures more difficult to obtain. (See Terra Tek paper at p. 3.) Since the Colpoys et al. propping agent has a similar high density, the same problems would be expected to be associated with its use. Additionally, sintered bauxite is relatively expensive. The cost per pound of bauxite is ten to fifteen times that of sand. (See Terra Tek paper at pp. 2–3 and McDaniel et al. at p. 4.) Accordingly, there has been a definite need for a lower density and less expensive propping agent having the mechanical strength to withstand closure pressures of 10,000 psi or greater.

SUMMARY OF THE INVENTION

It is, therefore, a main object of the present invention to provide a propping agent for hydraulic fracturing of subterranean formations which overcomes the above-mentioned drawbacks.

It is a more specific object of the present invention to provide a propping agent for hydraulic fracturing of subterranean formations which has sufficient mechanical strength to be able to withstand closure pressures of 10,000 psi or greater but also has a density of less than 3.0 gm/cc.

A further object of this invention is to provide a propping agent for use in hydraulic fracturing of subterranean formations which is less expensive than sintered bauxite propping agent.

Another object of this invention is to provide a propping agent for use in hydraulic fracturing of subterranean formations which requires lower viscosity fracturing fluids and lower pumping rates than sintered bauxite propping agent.

A still further object of this invention is to provide a propping agent for hydraulic fracturing of subterranean formations which facilitates fracture control and the obtaining of high conductivity fractures.

An additional object of this invention is to provide an economical alternative to sand for medium closure stress (6,000-10,000 psi) subterranean formations.

Additional objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of instrumentalities and combinations particularly pointed out in the appended claims.

To achieve the objects, and in accordance with the purpose of the invention, as embodied and broadly described herein, the invention comprises a high-strength propping agent for use in hydraulic fracturing of subterranean formations comprising solid, spherical particles, the particles having an alumina content of between 40 and 60%, a density of less than 3.0 gm/cc, and an ambient temperature permeability of 100,000 or more millidarcies at 10,000 psi.

To further achieve the objects in accordance with the purpose of the invention as embodied and broadly described herein, the invention comprises a hydraulic fracturing method in which a fluid is injected into a subterranean formation to open a fracture therein and a propping agent is placed in the formation to prop open the fracture, the propping agent being solid, spherical particles having an alumina content of between 40 and 60%, a density of less than 3.0 gm/cc, and an ambient temperature permeability of a 100,000 or more millidarcies at 10,000 psi.

The foregoing and other objects, features, and advantages of the present invention will be made more apparent from the following description of the preferred embodiment.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a plot of permeability versus closure stress for samples of sintered bauxite, Ottawa sand and the propping agent of the present invention tested under laboratory conditions.

FIG. **2** is a plot of conductivity decay from brine and high temperature exposure versus time for samples of sintered bauxite and the propping agent of the present invention tested under laboratory conditions.

FIG. **3** is a plot of conductivity decay from brine and high temperature exposure versus time for samples of Ottawa sand and the propping agent of the present invention tested under laboratory conditions.

FIG. **4** is a plot of conductivity versus closure stress at a flow rate of 1 Mscf/D for a concentration of 1 lb/ft^2 of the propping agent of the present invention and a concentration of 3 lb/ft^2 of Ottawa sand tested under laboratory conditions.

FIG. **5** is a plot of conductivity versus closure stress at a flow rate of 10 Mscf/D for a concentration of 1 lb/ft^2 of the propping agent of the present invention and a concentration of 3 lb/ft^2 of Ottawa sand tested under laboratory conditions.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference will now be made in detail to the present preferred embodiments of the invention.

A high strength propping agent for use in hydraulic fracturing of subterranean formations surrounding oil wells, gas wells and similar boreholes in accordance with the present invention comprises solid, spherical particles having an alumina content of between 40 and 60%, a density of less than 3.0 gm/cc, and an ambient temperature permeability of 100,000 or more millidarcies at 10,000 psi.

For purposes of the present invention the propping agent particles should have an alumina (Al_2O_3) content of between 40 and 60%, preferably between 45.5 and 60%, and a silica (SiO_2) content of between 36.5 and 56.5%, preferably between 36.5 and 51%. Good results have been obtained with material having the following composition (calcined basis):

SiO_2	45.8
Al_2O_3	50.7
TiO_2	2.60
Fe_2O_3	0.70
CaO	0.03
MgO	0.04
Na_2O	0.06
K_2O	0.05
Li_2O	0.02
Total	100.00

-continued

This material had a density of about 2.62–2.65 gm/cc.

In a preferred embodiment, the propping agent particles are made from Eufaula bauxite. The term "Eufaula bauxite" refers to a bauxitic-kaolin type material deposited in and around Eufaula, Ala. See Burst, J. F., "Genetic Relationship of the Andersonville, Georgia and Eufaula, Alabama Bauxitic-Kaolin Areas", Society of Mining Engineers, AIME Transactions, Vol. 246, pp. 137–144 (June 1974), which is incorporated by reference herein as background information. Preferably, the Eufaula bauxite will contain at least some (above 5%) gibbsite. The greater the gibbsite content the higher the loss on ignition. Preferably, the loss on ignition will be between 14.5 and 20%. Good results have been obtained with a gibbsite content yielding a loss on ignition of about 17.1%.

A small amount (up to 5%) of the Eufaula bauxite may be replaced with a crush strength enhancer selected from the group: nepheline syenite, fused bauxite dust, wollastonite, talc, and feldspar. Of these, nepheline syenite is the preferred crush strength enhancer. It is believed that addition of up to 5% of one of these crush strength enhancers will serve to impede cristobalite formation upon sintering of the raw material and thereby enhance the crushing strength of the final particles.

The propping agent particles of the present invention may be made by the methods disclosed in copending U.S. patent application No. 437,321 of Eugene Paul Lunghofer, Sten Mortensen, and Aubrey Ward, filed concurrently herewith on Oct. 28, 1982 for A Process For The Production Of Sintered Bauxite Spheres. As explained therein, an aqueous feed suspension comprising the bauxitic-kaolin type material and a suitable binder is prepared. The feed suspension is then continuously atomized into a layer of already partly dried particles fluidized in a stream of drying air. Particles are continually recovered from this layer and continuously separated into oversized, undersized, and product fractions, making allowance for anticipated shrinkage in the subsequent sintering operation. Undersized fractions, relatively fine product fractions, ground product fractions, and ground oversized product fractions are continuously recycled to the layer of fluidized particles at a substantial distance (measured along the flow path of the particles) from the site where the recovery of such particles takes place. The non-recycled product fractions are dried and sintered by heating at a temperature of between 1200° and 1650° C.

Propping agents made from the above-described materials and by the above-described methods will have a density of less than 3.0 gm/cc, thus, overcoming the disadvantages associated with the high-density sintered bauxite propping agent described above. Moreover, contrary to the teachings of Cooke et al., the lower density propping agent of the present invention has sufficient mechanical strength to withstand closure stresses of 10,000 psi or greater. The suitability of the propping agents of the present invention for such high closure stress applications is demonstrated by the comparative permeability testing described in Example 1:

EXAMPLE 1—Permeability

The permeability of a 20–40 mesh sample of the propping agent of the present invention was compared to a 20–40 mesh sample of sintered bauxite propping agent of the type described by Cooke et al. The propping agent of the present invention had the following composition (calcined basis):

SiO_2	45.80
Al_2O_3	50.70
TiO_2	2.60
Fe_2O_3	0.70
CaO	0.03
MgO	0.04
Na_2O	0.06
K_2O	0.05
Li_2O	20.02
Total	100.00

It had a density of about 2.62–2.65 gm/cc. The sintered bauxite propping agent was a commercial product obtained from The Norton Company. It had an alumina content of between 86 and 89% and a density of about 3.68–3.75 gm/cc.

Permeability was determined by pumping deionized water at a known rate through a known volume (70 ml loose) of each sample placed in a permeameter designed to stimulate a propped fracture. This was done at ambient temperature and at various closure stesses between 500 and 12,000 psi. A constant value of closure stress was maintained by a hydraulic press. The pressure drop across the simulated fracture was recorded as was the propped fracture thickness for each closure stress. The test results are graphically illustrated in FIG. 1. For additional comparison, the results of permeability testing on 20–40 mesh Ottawa sand is also plotted.

The permeability of the propping agent of the present invention decreases more rapidly with increasing closure stress than does the permeability of the sintered bauxite propping agent. Nevertheless, the propping agent of the present invention maintains a permeability of greater than 100,000 millidarcies at closure pressures of up to 10,000 psi. Even at 12,000 psi, the permeability of the propping agent of the present invention is still very high. These results indicate that the propping agent of the present invention is suitable for high closure stress gas and oil well applications.

Examples 2–4 illustrate that the propping agent of the present invention also meets the American Petroleum Institute's sand specifications for sieve analysis, sphericity and roundness evaluation, and crush resistance. Although Example 5 shows that the acid solubility of the propping agent of the present invention is just outside the American Petroleum Institute sand specifications, the brine exposure test reported in Examples 6 and 7 shows that the propping agent of the present invention has corrosive resistance of the same order as both sintered bauxite and Ottawa sand propping agents. (The American Petroleum Institute has not yet promulgated an official specification for sintered bauxite propping agent.)

EXAMPLE 2—Sieve Analysis

Samples of 100.0 gm of the materials tested in Example 1 were placed in a nest of sieves and shaken for 15 minutes using sieve sizes recommended by American Petroleum Institute procedures. The sample remaining

on each sieve was then weighed to determine the percent retained. The results were as follows:

	Percent Retained		
Sieve Size	Propping Agent of Present Invention	Sintered Bauxite	API Specifications (Sand)
16	0.00	0.00	— 0.00
20	0.00	8.33	
30	55.84	60.37	≧90.00
35	41.28	23.23	
40	2.82	7.66	
50	0.02	0.25	≦1.00
PAN	0.01	0.01	

EXAMPLE 3—Sphericity and Roundness Evaluation

Twenty particles of the materials tested in Example 1 were visually examined for sphericity and roundness using Krumbein's and Sloss' chart for visual estimation of roundness and sphericity. The results were as follows:

Sample	Sphericity	Roundness
Propping Agent of Present Invention	0.9	0.9
Sintered Bauxite	0.9	0.9
API Specification (Sand)	≧0.6	≧0.6

EXAMPLE 4—Crush Resistance

Forty-gram samples of a particular particle size of the materials tested in Example 1 were isolated and placed in a test cell. The cell was placed in a hydraulic press and 12,500 pounds of force was applied for two minutes. The samples were then sieved and the fines collected and weighed. The results were as follows:

Sample	Percent Crushable
Propping Agent of Present Invention	0.20
Sintered Bauxite	0.25
API Specification (Sand)	≦8.00

EXAMPLE 5—Acid Solubility

Samples of the materials tested in Example 1 were dried to a constant weight and 5 gm. were weighed to the nearest 0.1 mg. The sample was treated with 100 ml. of 12% HCl—3% HF in a water bath at 65.6° C. for 30–35 minutes. The samples were filtered, washed and dried to a constant weight. The weight loss was determined and computed as a percent. The results were as follows:

Sample	Percent Solubility
Propping Agent of Present Invention	2.99
Sintered Bauxite	1.39
API Specification (Sand)	<2.00

(Because of the small sample size, the precision of this test is questionable. For example, other tests with sintered bauxite propping agent have yielded a 7% acid solubility.)

EXAMPLE 6—Brine Exposure

20–40 mesh samples of the materials tested in Example 1 were placed in a test cell and heated to 250° F. For both propping agents, a concentration of 2 lb/ft^2 were used. A liquid brine solution was pumped through the propping agent at a constant rate for a period of 24 hours. The brine solution had the following ingredients: 8% NaCl and 2.5% CaCl. This solution was preheated to match the cell temperature of 250° F. The closure stress on the propping agents were maintained at a constant level of 8,000 psi throughout the test. During the entire test, the pressure drop through the propping agent was recorded in order to determine the permeability decay.

The results of the conductivity decay over time for these two materials is shown in FIG. **2**. The conductivities were normalized with respective initial conductivities to enable direct comparison. As can be seen from FIG. **2**, the percent decay in the conductivity of the propping agent of the present invention was slightly less than that of the sintered bauxite propping agent.

EXAMPLE 7—Brine Exposure

Tests similar to that of Example 6 were run with 20–40 mesh samples of the propping agent of the present invention tested in Example 1 and Ottawa sand at 4,000 psi. These results are graphically illustrated in FIG. **3**. As can be seen from FIG. **3**, the percent decay in conductivity is essentially identical for both the propping agent of the present invention and Ottawa sand.

In addition to being useful in hydraulic fracturing of high closure stress (10,000 psi or greater) subterranean formations, the propping agent of the present invention is also useful for medium closure stress (6,000–10,000 psi) applications. Not only will the propping agent of the present invention perform better than sand under such conditions, but also only one third as much propping agent is required. Thus, treatment of medium closure stress subterranean formations with the propping agent of the present invention is an economically feasible alternative to treatment with sand. Examples 8-10 illustrate the comparative effectiveness of the propping agent of the present invention and Ottawa sand at a concentration ratio of 1:3.

EXAMPLE 8

20–40 mesh samples of the propping agent of the present invention tested in Example 1 and Ottawa sand were placed in a test cell and heated to 250° F. at a closure stress of 1,000 psi. Preheated nitrogen at 100 psi was passed through the sample during this period. When the target test temperature was reached, gas flow rates were varied to produce superficial velocities from 1 cm/sec to 30 cm/sec. Gas temperatures at entrance and exit of cell along with cell temperature were recorded. Gas flow rate, sample height and pressure drop along 10 cm. cell length was measured. Each flow was allowed to reach steady state conditions before proceeding to the next flow rate. The above flow ranges were repeated for closure stresses of 2,000, 4,000, 6,000, 8,000 and 10,000 psi. The data was then analyzed producing values at each closure stress for Darcy permeability and conductivity at various flow rates, turbulence factor and absolute permeability. Flow rates were controlled by use of a metering valve placed at the exit of the cell, thus allowing test pressure to be controlled. Flow rates were measured at atmospheric conditions by a thermal flowmeter at high and medium rates and a rotometer for low flow rates. Gas flow rate and density at test conditions was calculated from atmospheric measurements assuming ideal gas behavior and using an average gas temperature pressure in the cell.

Tests were conducted using the propping agent of the present invention at concentrations of 0.5, 1.0 and 1.5 lb/ft^2, and Ottawa sand at concentrations of 1.5, 3.0 and 4.5 lb/ft^2. For the propping agent of the present invention the following results were obtained:

Concentration (lb/ft^2)	Closure Stress (psi)	Turbulence Factor $\left(\frac{\text{atm} - \text{sec}^2}{\text{gm}}\right)$	Conductivity (md/ft)	Permeability (md)	Predicted Beta $\left(\frac{\text{atm} - \text{sec}^2}{\text{gm}}\right)$
0.5	6,000	—	480	—	—
1.0	6,000	2.3×10^{-3}	1,550	139,000	1.3×10^{-3}
1.5	6,000	1.5×10^{-3}	2,270	139,000	1.3×10^{-3}
0.5	8,000	—	210	—	—
1.0	8,000	2.9×10^{-3}	1,030	89,300	2.6×10^{-3}
1.5	8,000	2.0×10^{-3}	1,210	78,000	3.2×10^{-3}
0.5	10,000	—	170	—	—
1.0	10,000	5.7×10^{-3}	520	52,600	6.0×10^{-3}
1.5	10,000	3.1×10^{-3}	750	55,000	5.5×10^{-3}

(Due to the difficulty of measuring sample height at low proppant concentrations, the permeability and turbulence factors for 0.5 lb/ft^2 tests are not reported.)

For Ottawa sand, the following data was obtained:

Concentration (lb/ft^2)	Closure Stress (psi)	Turbulence Factor $\left(\frac{\text{atm} - \text{sec}^2}{\text{gm}}\right)$	Conductivity (md/ft)	Permeability (md)	Predicted Beta $\left(\frac{\text{atm} - \text{sec}^2}{\text{gm}}\right)$
1.5	6,000	—	600	—	—
3.0	6,000	3.1×10^{-3}	1,070	44,000	7.7×10^{-3}
4.5	6,000	3.3×10^{-3}	2,000	106,300	2.0×10^{-3}
1.5	8,000	—	180	—	—
3.0	8,000	2.05×10^{-2}	550	22,520	2.2×10^{-2}
4.5	8,000	7.6×1^{-3}	600	18,500	2.9×10^{-2}
1.5	10,000	—	100	—	—
3.0	10,000	6.91×10^{-2}	200	8,620	9.6×10^{-2}
4.5	10,000	1.0×10^{-2}	280	10,700	6.8×10^{-2}

Because the effect of turbulence becomes more predominant at increasing velocities, it is not sufficient to compare absolute permeabilities and conductivities alone. Therefore, FIGS. **4** and **5** show Darcy conductivity at two different velocities, which would be encountered in fractured wells producing approximately 1,000 Mscf/D to 10,000 Mscf/D. These figures illustrate that at low flow rates the propping agent of the present invention. possesses a conductivity exceeding that of three times the concentration of sand at 6,000 psi and above, and at higher flow rates the propping agent of the present invention has a conductivity exceeding that of three times the concentration of sand at 6,500 psi and above.

EXAMPLE 9

20-40 mesh samples of the propping agent of the present invention tested in Example 1 and Ottawa sand were placed in a test cell in concentrations of 1 lb/ft^2 and 3 lb/ft^2, respectively. The test cell was set up as in Example 8. The closure stress was brought to 4,000 psi and the temperature of the cell increased to 250° F. Preheated nitrogen was flowed through the propping agent as previously described to determine the initial conductivity. Next, a solution of fracturing fluid, broken with an enzyme breaker, was pumped through the propping agent at a low, constant rate for a period of four hours. This simulated the initiation of the clean-up process. The fluid was preheated to approximately 250° F. The same volume of the broken fluid was pumped for each test. This was followed by preheated nitrogen to continue the simulation of the clean-up process. Pressure drop through the sample was monitored until it became a constant. At this time, various flow rates of nitrogen were used to determine the final permeability. The results were as follows:

Propping Agent	Conductivity Initial	(darcy-ft) Final
Propping Agent of Present Invention	1.46	0.20
Ottawa Sand	2.62	0.18

The initial conductivities correspond to measurements made prior to pumping the broken fracturing fluid. The final conductivities were measured after residue damage by the broken fracturing fluid had been accomplished. It is evident from these results that a very large amount of damage occurred in both tests. However, it is interesting to note that even though the conductivity of the propping agent of the present invention was initially much less than the Ottawa sand, the final conductivities were essentially equal. This indicates that less damage was actually incurred on the propping agent of the present invention than on the Ottawa sand.

EXAMPLE 10

Several cases were run on a single phase, two-dimensional, finite difference reservoir simulator. The effects of both formation properties and fracture properties were studied. For each set of formation and fracture properties, two cases were run: one with Ottawa sand as propping agent and another with the propping agent of the present invention tested in Example 1. The propping agent of the present invention was used at a 1:3 ratio (by weight) compared to Ottawa sand. The following properties were held constant for all simulations presented here:

1. New pay thickness = 125 ft.
2. Initial closure stress = 8000 psi
3. Initial reservoir pressure = 4000 psi
4. Gas gravity = 0.68
5. Well spacing = 640 acres
6. Minimum surface flowing pressure = 1000 psi

The sensitivity to (1) formation permeability, (2) proppant permeability damage by fluid residue, and (3) fracture length are presented in Table 1:

	Cumulative Production Improvement					
	@ 1 year		@ 7 years		@ 15 years	
	MMSCF	%	MMSCF	%	MMSCF	%
Case 1:						
Formation Perm = 0.008 md, Frac Length = 1600 ft. No Damage Initial Q = 3.5 MMSCF/D	0	0	10	0.2	93	1.6
Case 2:						
Formation Perm = 0.1 md, Frac Length = 1600 ft. 75% Damage Initial Q = 3.5 MMSCF/D	0	0	533	6.9	925	7.3
Case 3:						
Formation Perm = 0.1 md, Frac Length = 1100 ft. 50% Damage Initial Q = 3.5 MMSCF/D	0	0	315	3.8	775	5.7
Case 4:						
Formation Perm = 0.008 md, Frac Length = 1600 ft. No Damage Initial Q = 2 MMSCF/D	0	0	14	0.4	11	0.33

EXAMPLE 11

This Example illustrates a method of making the hydraulic fracturing propping agents of the present invention. It is also recorded as Example 3 of co-pending U.S. pat. application No. 437,321 of Eugene Paul Lunghofer, Sten Mortensen, and Aubrey Ward, filed concurrently herewith on Oct. 28, 1982 for A Process For The Production Of Sintered Bauxite Spheres.

The starting material in this example is a bauxitic-kaolin ore from Eufaula, Ala. having the following analysis by weight after ignition at 800° C.: Al_2O_3 50.7%; SiO_2 45.8%; TiO_2 2.60%; Fe_2O_3 0.71%; with the remainder being alkali and alkali-earth metal oxides. An aqueous dispersion of the material as mined is prepared using ball milling or mechanical agitation and addition of 0.25% "DARVAN C" or 0.2% sodium pyrophosphate. Water is added to a solids content of 45%. The pH is adjusted with NaOH to above 8 to insure complete deflocculation and low viscosity. 0.75% "GELVATOL" 20/30 is added as a temporary binder.

This feed, in an amount of 4,000 kg/hour, is passed through pressure nozzles in a fluid bed unit having a fluidizing area of 3 m.^{2}. The velocity of the fluidizing air is 1.2 m/sec, the inlet temperature of the air is 550° C., and the outlet temperature of the air is 70° C. Recycled material introduced through a powder inlet amounts to 1700 kg/hour. The height of the fluidized particle layer is approximately 35 cm. The average residence time of the particles in the fluidized layer is about 15 minutes.

Material is withdrawn in a quantity of 3400 kg/hour, which by sieving is separated into: an oversized fraction having a particle size of about 2.1 mm (50 kg/hour); a course product fraction having a particle size of between 1.2 and 2.1 mm (300 kg/hr); a fine product fraction having a particle size of between 0.6 and 1.2 mm (2450 kg/hour); and an undersized fraction having a particle size below 0.6 mm (600 kg/hour). Also in a bag filter collector unit 300 kg/hour entrained particles are collected and recycled to the tank holding the feed.

The total amount of the oversized fraction together with 400 kg/hour of the fine product fraction is ground in a grinding unit having a sieve of mesh size 3,000 microns, and together with the undersized fraction is lead to the fluid bed unit as seed or nuclei particles. 650 kg/hour of the fine product fraction is recycled without prior grinding.

The remaining material from the product fractions is led through an oven in which the remaining moisture and organic additions (approximately 4% by weight) are removed. The material is then sintered in a rotary kiln at a temperature of approximately 1500° C. for approximately 10 minutes. The sintered particles are then subjected to a further sieving operation to assure that substantially all of the product has the appropriate particle size.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided that they come within the scope of the appended claims and their equivalents.

What is claimed is:

1. In a hydraulic fracturing method in which a fluid is injected into a subterranean formation to open a fracture therein, the improvement wherein said fracture is propped open with a high strength propping agent comprising solid, spherical particles, said particles having an alumina content of between 40 and 60%, a density of less than 3.0 gm/cc, and an ambient temperature permeability of 100,000 or more millidarcies at 10,000 psi.

2. The hydraulic fracturing method of claim 1 wherein the subterranean formation is a high closure stress (10,000 psi or greater) formation.

3. The hydraulic fracturing method of claim 1 wherein the subterranean formation is a medium closure stress (6,000-10,000 psi) formation.

* * * * *

EXHIBIT 11

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SECURITIES AND EXCHANGE COMMISSION
WASHINGTON, D.C. 20549

FORM 10-K

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FOR THE FISCAL YEAR ENDED DECEMBER 31, 2002

[ ] TRANSITION REPORT PURSUANT TO SECTION 13 OR 15(d) OF THE SECURITIES EXCHANGE ACT OF 1934
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COMMISSION FILE NO. 0-28178

CARBO CERAMICS INC.
(Exact name of registrant as specified in its charter)

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DELAWARE	72-1100013
(State or other jurisdiction of incorporation or organization)	(I.R.S. Employer Identification Number)

</Table>

6565 MACARTHUR BOULEVARD
SUITE 1050
IRVING, TEXAS 75039
(Address of principal executive offices)

(972) 401-0090
(Registrant's telephone number)

SECURITIES REGISTERED PURSUANT TO SECTION 12(b) OF THE ACT: NONE

SECURITIES REGISTERED PURSUANT TO SECTION 12(g) OF THE ACT:
COMMON STOCK, PAR VALUE $0.01 PER SHARE
PREFERRED STOCK PURCHASE RIGHTS

Indicate by check mark whether the registrant (1) has filed all reports required to be filed by Section 13 or 15(d) of the Securities Exchange Act of 1934 during the preceding 12 months (or for such shorter period that the registrant was required to file such reports), and (2) has been subject to such filing requirements for the past 90 days. Yes [X] No [ ]

Indicate by check mark if disclosure of delinquent filers pursuant to Item 405 of Regulation S-K is not contained herein, and will not be contained, to the best of registrant's knowledge, in definitive proxy or information statements incorporated by reference in Part III of this Form 10-K or any amendment to this Form 10-K. [ ]

Indicate by check mark whether the registrant is an accelerated filer (as defined in Rule 12b-2 of the Act). Yes [X] No [ ]

The aggregate market value of the voting stock held by non-affiliates of the Registrant, based upon the closing sale price of the Common Stock on February 28, 2003, as reported on the New York Stock Exchange, was approximately $228,702,035. Shares of Common Stock held by each officer and director and by each person who owns 5% or more of the outstanding Common Stock have been excluded in that such persons may be deemed to be affiliates. This determination of affiliate status is not necessarily a conclusive determination for other purposes.

As of February 28, 2003, Registrant had outstanding 15,483,836 shares of Common Stock.

DOCUMENTS INCORPORATED BY REFERENCE

Portions of the Proxy Statement for Registrant's Annual Meeting of Shareholders to be held April 8, 2003 are incorporated by reference in Parts II and III.

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PART I

ITEM 1. BUSINESS

GENERAL

CARBO Ceramics Inc. ("the Company") was formed in 1987 to acquire the assets of Standard Oil Proppants Company, LP, a joint venture between two ceramic proppant manufacturers. Since its founding in 1987, CARBO Ceramics has become the world's largest producer and supplier of ceramic proppant for use in the hydraulic fracturing of natural gas and oil wells. Demand for ceramic proppant depends primarily upon the demand for natural gas and oil and on the number of natural gas and oil wells drilled, completed or recompleted worldwide. More specifically, the demand for ceramic proppant is dependent on the number of oil and gas wells that are hydraulically fractured to stimulate production.

Hydraulic fracturing is the most widely used method of increasing production from oil and gas wells. The hydraulic fracturing process consists of pumping fluids down a natural gas or oil well at pressures sufficient to create fractures in the hydrocarbon-bearing rock formation. A granular material, called proppant, is suspended and transported in the fluid and fills the fracture, "propping" it open once high-pressure pumping stops. The proppant-filled fracture creates a permeable channel through which the hydrocarbons can flow more freely from the formation to the well and then to the surface.

There are three primary types of proppant that can be utilized in the hydraulic fracturing process: sand, resin-coated sand and ceramic. Sand is the least expensive proppant, resin-coated sand is more expensive and ceramic proppant is typically the highest cost. The higher initial cost of ceramic proppant is justified by the fact that the use of these proppants in certain well conditions results in increased production of oil and gas and increased cash flow for the operators of oil and gas wells. The increased production rates are primarily attributable to the higher strength and more uniform size and shape of ceramic proppant versus alternative materials.

Based on the Company's internally generated market information and information contained in the United States Geological Survey Minerals Yearbook, the Company estimates that it supplies approximately 56% of the ceramic proppant and 9% of all proppant used worldwide. During the year ended December 31, 2002, the Company generated approximately 70% of its revenues in the U.S. and 30% in international markets.

In May 2002, the Company expanded its business through the acquisition of Pinnacle Technologies, Inc. ("Pinnacle"). Pinnacle is the world's leading provider of fracture mapping services, and its fracture simulation software FracproPT(R) is the most widely used model in the world. For the year ended December 31, 2002, Pinnacle accounted for less than 5% of the Company's total revenues.

PRODUCTS

The Company manufactures four distinct ceramic proppants. CARBOHSP(TM)2000 and CARBOPROP(R) are premium priced, high strength proppants designed primarily for use in deep gas wells. CARBOHSP(TM)2000 was introduced in January 2000 and is an improved version of CARBOHSP(TM), which was introduced in 1979 as the original ceramic proppant. CARBOHSP(TM)2000 has the highest strength of the ceramic proppant manufactured by CARBO Ceramics and is used primarily in the fracturing of deep gas wells. CARBOPROP(R), which was introduced by the Company in 1982, is slightly lower in weight and strength than CARBOHSP(TM)2000 and was developed for use in deep gas wells that do not require the strength of CARBOHSP(TM)2000.

The CARBOLITE(R) and CARBOECONOPROP(R) products are lightweight proppants designed for use in gas wells of moderate depth and shallower oil wells. CARBOLITE(R), introduced in 1984, is used in medium depth oil and gas wells, where the additional strength of ceramic proppant may not be essential, but where higher production rates can be achieved due to the product's roundness and uniform grain size. CARBOECONOPROP(R), introduced in 1992 to compete directly with sand-based proppant, has been the Company's lowest priced and fastest growing product. The introduction of CARBOECONOPROP(R) has resulted in ceramic proppant being used by operators of oil and gas wells that had not previously used

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ceramics. The Company believes that many of the users of CARBOECONOPROP(R) had previously used sand or resin-coated sand.

COMPETITION AND MARKET SHARE

The Company's chief worldwide competitor is Norton Proppants ("Norton"). Norton is owned by Compagnie de Saint-Gobain, a large French glass and materials company. Norton manufactures ceramic proppants that directly compete with each of the Company's products. In addition, Mineracao Curimbaba ("Curimbaba"), based in Brazil, manufactures a sintered bauxite product similar to the Company's CARBOHSP(TM), which is marketed in the United States under the name "Sinterball". Curimbaba has notified the Company that it intends to introduce an intermediate strength ceramic proppant similar to the Company's CARBOPROP(R) although the Company believes that it would be difficult for Curimbaba to introduce such a product that does not infringe patents held by the Company and Norton. The Company believes that Curimbaba has not expanded its U.S. product line to include a lightweight ceramic proppant and is unlikely to do so in light of patents held by the Company. The Company is also aware of Borovichi Refractories, a manufacturer of ceramic proppant located in Russia about which the Company has limited information. The Company believes that Borovichi to date has sold its product solely within Russia.

Competition for CARBOHSP(TM)2000 and CARBOPROP(R) principally includes ceramic proppant manufactured by Norton and Curimbaba. The Company's CARBOLITE(R) and CARBOECONOPROP(R) products compete with ceramic proppant produced by Norton and with sand-based proppant for use in the hydraulic fracturing of medium depth natural gas and oil wells. The leading suppliers of mined sand are Unimin Corp., Badger Mining Corp., Fairmount Minerals Limited, Inc. and Ogelbay-Norton Company. The leading suppliers of resin-coated sand are Borden Chemical, Inc. Oilfield Products Group and Santrol, a subsidiary of Fairmount Minerals.

The Company believes that the most significant factors that influence a customer's decision to purchase the Company's products are (i) price/performance ratio, (ii) on-time delivery performance, (iii) technical support and (iv) proppant availability. The Company believes that its products are competitively priced and that its delivery performance is excellent. The Company also believes that its superior technical support has enabled it to persuade customers to use ceramic proppant in an increasingly broad range of applications and thus increased the overall market for the Company's products. Since 1993, the Company has consistently expanded its manufacturing capacity and plans to continue its strategy of adding capacity to meet anticipated future increases in sales demand.

The Company continually conducts testing and development activities with respect to alternative raw materials to be used in the Company's existing and alternative production methods. The Company is not aware of the development of alternative products for use as proppant in the hydraulic fracturing process. The Company believes that the main barriers to entry for additional competitors are the patent rights held by the Company and certain of its current competitors, the "know-how" and trade secrets necessary to manufacture a competitive product and the capital costs involved in building production facilities of sufficient size to be operated efficiently.

CUSTOMERS AND MARKETING

The Company's largest customers are, in alphabetical order, BJ Services Company, Halliburton Energy Services, Inc. and Schlumberger, the three largest participants in the worldwide petroleum pressure pumping industry. These companies collectively accounted for approximately 79% of the Company's 2002 revenues and approximately 81% of the Company's 2001 revenues. However, the end users of the Company's products are the operators of natural gas and oil wells that hire the pressure pumping service companies to hydraulically fracture wells. The Company works both with the pressure pumping service companies and directly with the operators of natural gas and oil wells to present the technical and economic advantages of using ceramic proppant. The Company generally supplies its customers with products on a just-in-time basis, with transactions governed by individual purchase orders. Continuing sales of product depend on the Company's direct customers and the well operators being satisfied with both product quality and delivery performance.

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The Company recognizes the importance of a technical marketing program when selling a product that offers financial benefits over time but is initially more costly than alternative products. The Company must market its products both to its direct customers and to owners and operators of natural gas and oil wells. The Company's sales and marketing staff regularly calls on and keeps close contact with the people who are influential in the proppant purchasing decision: production companies, regional offices of oilfield service companies that offer pressure pumping services and various completion engineering consultants. Beginning in 1999, the Company increased its marketing efforts to production companies. The Company expanded its technical sales force in recent years and plans to continue to increase its efforts to educate end users on the benefits of using ceramic proppant. While the Company's products have historically been used in very deep wells that require high-strength proppant, the Company believes that there is economic benefit to well operators of using ceramic proppant in shallower wells that do not necessarily require a high-strength proppant. The Company believes that its education-based technical marketing efforts will allow it to capture a greater portion of the large market for sand-based proppant over time. The Company currently provides a variety of technical support services and has developed computer software that models the return on investment achievable by using the Company's ceramic proppant versus other proppant in the hydraulic fracturing of a natural gas or oil well.

The Company's worldwide sales and marketing activities are coordinated by its North American and International Marketing Managers. The Company's export marketing efforts in 2002 were conducted through its sales office in Aberdeen, Scotland and through commissioned sales agents located in South America, China and Australia.

The Company's products and services are used worldwide by U.S. customers operating abroad and by foreign customers. Sales outside the United States accounted for 30%, 27% and 37% of the Company's sales for 2002, 2001 and 2000, respectively. The distribution of the Company's export and domestic revenues is shown below, based upon the region in which the customer used the products and services:

<Table>
<Caption>

LOCATION	2002	2001	2000
	($ IN MILLIONS)		
<S>	<C>	<C>	<C>
United States	$ 88.0	$100.4	$58.9
International	38.3	36.8	34.4
Total	$126.3	$137.2	$93.3

</Table>

DISTRIBUTION

The Company maintains finished goods inventories at its plants in New Iberia, Louisiana, Eufaula, Alabama, and McIntyre, Georgia, and at eleven remote stocking facilities located in Rock Springs, Wyoming; Oklahoma City, Oklahoma; San Antonio, Texas; Fairbanks, Alaska; Edmonton, Alberta, Canada; Grande Prairie, Alberta, Canada; Rotterdam, The Netherlands; Jebel Ali, United Arab Emirates; Adelaide, Australia; Shanghai, China; and Singapore. The North American remote stocking facilities consist of bulk storage silos with truck trailer loading facilities. The Company owns the facilities in San Antonio, Rock Springs, Edmonton and Grande Prairie and subcontracts the operation of the facilities and transportation to a local trucking company in each location. The remaining North American stocking facilities are owned and operated by local companies under contract with the Company. International sites are duty-free warehouses operated by independent owners. North American sites are typically supplied by rail and international sites are typically supplied by container ship. In total, the Company leases 216 rail cars for use in the distribution of its products. The price of the Company's products sold for delivery in the lower 48 United States and Canada includes just-in-time delivery of proppant to the operator's well site, which eliminates the need for customers to maintain an inventory of ceramic proppant.

RAW MATERIALS

Ceramic proppant is made from alumina-bearing ores (commonly referred to as bauxite, bauxitic clay or kaolin, depending on the alumina content), that are readily available on the world market. Bauxite is largely

used in the production of aluminum metal, refractory material and abrasives. The main deposits of alumina-bearing ores in the United States are in Arkansas, Alabama and Georgia; other economically mineable deposits are located in Australia, Brazil, China, Jamaica, Russia and Surinam.

For the production of CARBOHSP(TM)2000, the Company uses calcined, abrasive-grade bauxite imported from Australia, and typically purchases its annual requirements at the seller's current prices. The Company has entered into an agreement with a supplier to supply its anticipated need for this ore through 2005. For the production of CARBOPROP(R), the Company uses a variety of materials that meet specific chemical and mineralogical requirements. Raw material for the production of CARBOPROP(R) may be either as-mined bauxitic clays or a blend of bauxite and kaolin, either of which is readily available to the Company at sellers' current prices or through long-term contracts.

The Company's Eufaula facility exclusively employs locally mined uncalcined kaolin for the production of CARBOLITE(R) and CARBOECONOPROP(R). The Company has entered into a contract that requires a supplier to sell to the Company up to 200,000 net tons of kaolin per year and the Company to purchase from the supplier 80% of the Eufaula facility's annual kaolin requirements through 2003. This agreement, which had an original term of ten years, stipulates a fixed price, subject to annual adjustment. A renewal or extension of this agreement is currently being negotiated.

The Company's production facility in McIntyre, Georgia uses locally mined uncalcined kaolin for the production of CARBOECONOPROP(R). During 2002, the Company acquired on both a fee simple and leasehold basis, acreage in Wilkinson County, Georgia which contains approximately 13 million tons of raw material suitable for production of CARBOLITE(R) and CARBOECONOPROP(R). At current production rates, the acquired raw material would supply the needs of the McIntyre facility for a period in excess of 100 years. The Company is currently evaluating the suitability of the raw material for the production of CARBOLITE(R) and CARBOECONOPROP(R) at its Eufaula, Alabama facility. The Company has entered into a long-term agreement with a third party to mine and transport this material at a fixed price subject to annual adjustment. The agreement requires the Company to utilize the third party to mine and transport at least 80% of the McIntyre facility's annual kaolin requirement.

The Company's production facility in Luoyang, China uses locally mined uncalcined kaolin and bauxite for the production of CARBOPROP(R) and CARBOLITE(R). Each of these materials is purchased under long term contracts with a minimum term of five years. The contracts stipulate a fixed price subject to annual adjustment. Under the terms of the agreements, the Company has an obligation to purchase, in total, a minimum of 10,000 metric tons per year.

PRODUCTION PROCESS

Ceramic proppants are made by grinding or dispersing ore to a fine powder, combining the powder into small, green (i.e., unfired) pellets and sintering the pellets at 2,500(LOGO)F to 3,000(LOGO)F in a rotary kiln.

The Company uses two different methods to produce ceramic proppant. The Company's plants in New Iberia, Louisiana, McIntyre, Georgia, and Luoyang, China use a dry process (the "Dry Process") which starts with bauxite, bauxitic clay or kaolin that has been dried to remove both free water and water which was chemically bound within the ore. This drying process is referred to as calcining. The Company has calcining facilities at its McIntyre, Georgia and Luoyang, China plants. Once the raw material is calcined, the ore is ground to a very fine powder. Pellets are then formed by combining the powder with water and binders and introducing the mixture into high-shear mixers. The process is completed once these pellets are sintered in a rotary kiln. The Company believes its competitors also use the Dry Process to produce ceramic proppant.

The Company's plant in Eufaula, Alabama, uses a wet process (the "Wet Process"), which starts with moist, uncalcined kaolin from local mines. The kaolin is dispersed with chemicals in a water slurry. With an atomizer, the slurry is sprayed into a dryer that causes the slurry to harden into green pellets. These green pellets are then sintered in rotary kilns. The Company believes that the Wet Process is unique to its plant in Eufaula, Alabama.

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PATENT PROTECTION

The Company makes ceramic proppant by processes and techniques that involve a high degree of proprietary technology, some of which are protected by patents.

The Company owns six U.S. patents and three foreign patents. Two of these U.S. patents and two of these foreign patents relate to the CARBOPROP(R) product. One of these U.S. patents and one of these foreign patents relate to the CARBOLITE(R) and CARBOECONOPROP(R) products. The Company's U.S. patents relating to the CARBOPROP(R) product expire in 2006. The Company's U.S. patent relating to the CARBOLITE(R) and CARBOECONOPROP(R)products expire in 2009. The three foreign patents cover various products in Canada, Mexico and Argentina and do not have a significant effect on the Company's business.

The Company believes that its patents have been and will continue to be important in enabling the Company to compete in the market to supply proppant to the natural gas and oil industry. The Company intends to enforce and has in the past vigorously enforced its patents. The Company may be involved from time to time in the future, as it has been in the past, in litigation to determine the enforceability, scope and validity of its patent rights. Past disputes with its main competitor have been resolved in settlements that permit the Company to continue to benefit fully from its patent rights. The Company and this competitor have cross-licensed certain of their respective patents relating to intermediate and low density proppant on both a royalty-free and royalty-bearing basis. Royalties under these licenses are not material to the Company's financial results. As a result of these cross licensing arrangements, the Company is able to produce a broad range of ceramic proppant while third parties are unlikely to be able to produce certain of these ceramic proppant without infringing on the patent rights held by the Company, its main competitor or both.

Pinnacle owns one U.S. patent application (together with a number of counterparts to that application in numerous foreign jurisdictions) that covers certain of its proprietary systems. The patent application is in the early stages of the patent prosecution process, and a patent may not issue on such application in any jurisdiction for some time, if it issues at all. Pinnacle also licenses several patents from third parties for use in its business. In addition to patent rights, Pinnacle uses a significant amount of know-how and other proprietary technology in the conduct of its business, and a substantial portion of this know-how and technology is licensed by Pinnacle from third parties.

PRODUCTION CAPACITY

The Company believes that constructing adequate capacity ahead of demand while incorporating new technology to reduce manufacturing costs are important competitive strategies to increase its overall share of the market for proppant. Prior to 1993, the Company's production capacity was substantially in excess of its sales requirements. Since that time, the Company has been expanding its capacity in order to meet the generally increasing demand for its products. In 1993, the Company increased the capacity of the Eufaula facility from 90 million pounds per year to 170 million pounds per year, in response to the increasing demand for the Company's CARBOLITE(R) and CARBOECONOPROP(R) products. In 1995, the Company completed a 40 million-pound per year capacity expansion at the New Iberia facility, intended to meet increasing demand for CARBOHSP(TM) and CARBOPROP(R). In 1996, the Company commenced operation of its second 80 million-pound per year expansion of the Eufaula plant bringing total capacity at the facility to 250 million pounds per year. In late 2002, the Company installed additional equipment in its New Iberia facility to increase production and provide additional capacity for research and development work. Upon completion of the New Iberia project in early 2003, total annual capacity at the facility will be 120 million pounds.

In June 1999, the Company substantially completed construction of a new manufacturing facility in McIntyre, Georgia. Design capacity of the plant is 200 million pounds per year and the total initial cost of the plant was approximately $60 million. The plant consists of two distinct production lines housed in a single building. Initial production was generated from the first production line in June 1999 and full design throughput was achieved on that line in November 1999. Initial production from the second production line began in December 1999 and the plant operated at approximately 61% of its design capacity in 2000 and 88% in 2001. During 2002, the Company spent approximately $15 million to expand the capacity of the McIntyre facility. Total spending for this project is projected to be approximately $17 million. Upon the anticipated completion of this expansion project in early 2003, total annual capacity at the McIntyre facility is expected to be 275 million pounds.

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In September 2002, the Company completed construction of a new manufacturing facility in Luoyang, China. The plant began operation on schedule in the fourth quarter of 2002. The total cost of the plant was approximately $10 million and the plant is expected to have annual production capacity of 40 million pounds. The first saleable product was produced from the plant in January 2003.

The following table sets forth the expected capacity of each of the Company's existing manufacturing facilities following completion of the expansions described above:

<Table>
<Caption>

LOCATION	ANNUAL CAPACITY	PRODUCTS
	(MILLIONS OF POUNDS)	
<S>	<C>	<C>
New Iberia, Louisiana.........	120	CARBOHSP(TM)2000 and CARBOPROP(R)
Eufaula, Alabama..............	250	CARBOLITE(R) and CARBOECONOPROP(R)
McIntyre, Georgia............	275	CARBOLITE(R), CARBOECONOPROP(R) CARBOHSP(TM)2000 and CARBOPROP(R)
Luoyang, China................	40	CARBOPROP(R) and CARBOLITE(R)

</Table>

The Company generally supplies its customers with products on a just-in-time basis and operates without any material backlog.

ENVIRONMENTAL AND OTHER GOVERNMENTAL REGULATIONS

The Company believes that its operations are in substantial compliance with applicable federal, state and local environmental and safety laws and regulations. The Company does not anticipate any significant expenditures in order to continue to comply with such laws and regulations.

EMPLOYEES

At December 31, 2002, the Company had 319 full-time employees. In addition to the services of its employees, the Company employs the services of consultants as required. The Company's employees are not represented by labor unions. There have been no work stoppages or strikes during the last three years that have resulted in the loss of production or production delays. The Company believes its relations with its employees are satisfactory.

FORWARD-LOOKING INFORMATION

The Private Securities Litigation Reform Act of 1995 provides a "safe harbor" for forward-looking statements. This Form 10-K, the Company's Annual Report to Shareholders, any Form 10-Q or any Form 8-K of the Company or any other written or oral statements made by or on behalf of the Company may include forward-looking statements which reflect the Company's current views with respect to future events and financial performance. The words "believe", "expect", "anticipate", "project" and similar expressions identify forward-looking statements. Readers are cautioned not to place undue reliance on these forward-looking statements, each of which speaks only as of the date the statement was made. The Company undertakes no obligation to publicly update or revise any forward-looking statements, whether as a result of new information, future events or otherwise. The Company's forward-looking statements are based on assumptions that we believe to be reasonable but that may not prove to be accurate. All of the Company's forward-looking information is subject to risks and uncertainties that could cause actual results to differ materially from the results expected. Although it is not possible to identify all factors, these risks and uncertainties include the risk factors discussed below.

The Company's results of operations could be adversely affected if its business assumptions do not prove to be accurate or if adverse changes occur in the Company's business environment, including but not limited to the potential declines in the demand for oil and natural gas; potential declines or increased volatility in oil

and natural gas prices that would adversely affect our customers, the energy industry or our production costs; potential reductions in spending on exploration and development drilling in the oil and natural gas industry that would reduce demand for our products and services; the development of alternative stimulation techniques; and the development of alternative proppants for use in hydraulic fracturing. The Company's results of operations could also be adversely affected if adverse changes occur in general global economic and business conditions or as a result of worldwide economic, political and military events, including war, terrorist activity or initiatives by the Organization of the Petroleum Exporting Countries.

AVAILABLE INFORMATION

The Company's annual reports on Form 10-K, quarterly reports on Form 10-Q, current reports on Form 8-K and amendments to those reports filed or furnished pursuant to Section 13(a) or 15(d) of the Exchange Act are made available free of charge on the Company's internet website at http://www.carboceramics.com as soon as reasonably practicable after it electronically files such material with, or furnishes it to, the Securities and Exchange Commission.

ITEM 2. PROPERTIES

The Company maintains its corporate headquarters (approximately 5,000 square feet of leased office space) in Irving, Texas, owns its manufacturing facilities, land and substantially all of the related production equipment in New Iberia, Louisiana, and Eufaula, Alabama, and leases its McIntyre, Georgia, facility through 2009 at which time title will be conveyed to the Company. The Company owns the buildings and production equipment at its facility in Luoyang, China and has been granted use of the land on which the facility is located for fifty years under the terms of a land use agreement with the People's Republic of China.

The facility in New Iberia, Louisiana, located on 24 acres of land owned by the Company, consists of two production units (approximately 85,000 square feet), a laboratory (approximately 4,000 square feet) and an office building (approximately 3,000 square feet). The Company also owns an 80,000 square foot warehouse on the plant grounds in New Iberia, Louisiana.

The facility in Eufaula, Alabama, located on 14 acres of land owned by the Company, consists of one production unit (approximately 111,000 square feet), a laboratory (approximately 2,000 square feet) and an office (approximately 1,700 square feet).

The facility in McIntyre, Georgia includes real property, consisting of approximately 36 acres, plant and equipment that are leased by the Company from the Development Authority of Wilkinson County. The term of the lease commenced on September 1, 1997 and terminates on January 1, 2009. Under the terms of the lease, the Company was responsible for all costs incurred in connection with the premises, including costs of construction of the plant and equipment. As an inducement to locate the facility in Wilkinson County, Georgia, the Company received certain ad-valorem property taxes incentives. The "net" lease provides for annual lease payments in lieu of ad-valorem property taxes. The total of all lease payments is immaterial in relation to the cost of the facility borne by the Company. At the termination of the lease, title to all of the real property, plant and equipment will be conveyed to the Company in exchange for nominal consideration. The Company has the right to purchase the property, plant and equipment at any time during the term of the lease for a nominal price.

The facility in Luoyang, China is located on approximately 9 acres and consists of various production and support buildings (approximately 106,000 square feet), a laboratory (approximately 6,000 square feet) and an office building (approximately 6,000 square feet).

The Company's customer service and distribution operations are located at the New Iberia facility, while its quality control, testing and development functions operate at the New Iberia, Eufaula and McIntyre facilities. The Company owns distribution facilities in San Antonio, Texas, Rock Springs, Wyoming, Edmonton and Grande Prairie, Alberta, Canada.

During the third quarter of 2002, the Company completed the acquisition of approximately 1,500 acres of land and leasehold interests in Wilkinson County, Georgia, near its plant in McIntyre, Georgia. The land

contains approximately 13 million tons of raw material for use in the production of the Company's lightweight ceramic proppants. The Company has contracted with a third party to mine and haul the reserves and bear the responsibility for subsequent reclamation of the mined areas.

The Company's wholly-owned subsidiary, Pinnacle Technologies, Inc., leases its corporate headquarters in San Francisco, California (approximately 6,800 square feet) and maintains leased offices totaling approximately 23,000 square feet in Houston, Texas; Centennial, Colorado; Delft, The Netherlands; and Calgary, Alberta, Canada. Pinnacle also owns an office condominium (approximately 2,800 square feet) in Bakersfield, California.

ITEM 3. LEGAL PROCEEDINGS

On October 28, 2002, a state court jury in Texas found the Company liable for tortious interference with a contract between Proppant Technology, Inc. and its supplier. On November 22, 2002, a judgment in the amount of $993,000 was entered in this case. The Company believes that it did not act improperly in this matter but has decided to appeal only the amount of the judgment.

From time to time, the Company is the subject of legal proceedings arising in the ordinary course of business. The Company does not believe that any of these proceedings will have a material adverse effect on its business or its results of operations.

ITEM 4. SUBMISSION OF MATTERS TO A VOTE OF SECURITY HOLDERS

No matters were submitted to a vote of security holders during the fourth quarter of fiscal year 2002.

EXECUTIVE OFFICERS OF THE REGISTRANT

Dr. C. Mark Pearson (age 47) has served as President and Chief Executive Officer since April 2001. Dr. Pearson joined the Company as Vice President of Marketing and Technology in March 1997. Prior to joining the Company, Dr. Pearson served as Associate Professor of Petroleum Engineering at the Colorado School of Mines from December 1995 and held various engineering and management positions with Atlantic Richfield Company from 1984 through December 1995.

Paul G. Vitek (age 44) has been the Senior Vice President of Finance and Administration and Chief Financial Officer since January 2000. Prior to serving in his current capacity, Mr. Vitek served as Vice President of Finance from February 1996 and has served as Treasurer and Secretary of the Company since 1988.

Mark L. Edmunds (age 47) has been the Vice President, Operations since April 2002. From 2000 until joining the Company, Mr. Edmunds served as Business Unit Manager and Plant Manager for FMC Corporation. Prior to 2000 Mr. Edmunds served Union Carbide Corporation and The Dow Chemical Company in a variety of management positions including Director of Operations, Director of Internal Consulting and Manufacturing Operations Manager.

Christopher A. Wright (age 38) has been a Vice President of the Company

EXHIBIT 12

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<DESCRIPTION>MINING AGREEMENT DATED AS OF JANUARY 1, 2003
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EXHIBIT 10.8*

MINING AGREEMENT

THIS AGREEMENT (herein called "Agreement") made as of January 1, 2003, between Arcilla Mining & Land Co., a corporation organized and existing under the laws of the state of Georgia and having an office at P.O. Box 1371, Milledgeville, Georgia 31061 ("Contractor"), and CARBO Ceramics Inc., a corporation organized and existing under the laws of the state of Delaware and having an office at 6565 MacArthur Boulevard, Suite 1050, Irving, Texas 75039 ("Owner").

WITNESSETH:

WHEREAS, Contractor and Owner desire to enter into this Agreement which will (i) supercede and replace the Raw Materials Requirements Agreement entered into between Contractor and Owner dated November 18, 1997, and (ii) set out the terms pursuant to which Contractor shall mine (either from lands owned or leased by Owner (the "Owner's Lands") or from lands owned or leased by Contractor as described on Exhibits B, C, D and E hereto (the "Contractors' Lands") and deliver to Owner's Wilkinson County, Georgia manufacturing plant a supply of kaolin, a naturally occurring mineral more particularly described (and meeting the specifications set forth) in Exhibit A hereto (the "Product"), and,

WHEREAS, Contractor is able and desires to mine and deliver such Product to Owner;

NOW, THEREFORE, in consideration of the mutual covenants and promises contained herein, the parties agree as follows:

1. TERM

The term of this Agreement shall be 20 years commencing January 1, 2003, and ending December 31, 2022.

2. CONTRACTOR'S RESPONSIBILITIES

Contractor shall be specifically responsible for the following (herein called the "Work"):

A. Obtaining and maintaining a valid mining permit from the State of Georgia and any other governmental body which requires Contractor to have a license or permit to mine and remove Product from the Subject Properties pursuant to this Agreement.

* Confidential Information in this Exhibit 10.8 has been omitted and filed separately with the Securities and Exchange Commission.

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B. Removing overburden from the Subject Properties in a manner so as to allow Owner unimpeded access to a minimum of 40,000 tons of Product at any given time.

C. Maintaining roads to, from and across the Subject Properties in a manner suitable to mine and remove from the Subject Properties the Product described in this Contract.

D. Reclaiming the Subject Properties in accordance with the permit(s) Contractor has obtained.

E. Providing to Owner a site of location, size and character upon which to stockpile approximately 5,000 tons of the Product. Seller shall maintain such stockpile at all times during this Agreement.

F. Contractor shall mine sufficient quantities of the Product to fill orders made by Owner on an "as needed" basis.

G. Contractor shall deliver to the Owner's manufacturing plant (the "Plant") in Wilkinson County, Georgia the quantities of the Product ordered by Owner. If Owner requests delivery to any location other than the Plant, Owner shall bear all costs for transportation in excess of the cost to transport the Product to the Plant.

3. Purchase Commitment

A. In each year during the term of this Agreement, Owner shall be obligated to accept deliveries of conforming Product from Contractor totaling, as a minimum, eighty percent (80%) of its actual annual requirements of the Product during such year for its operations in Wilkinson County, Georgia. In the event Contractor fails to deliver Product in a timely manner which has been ordered by Owner and Owner purchases such Product from another source or contracts with another contractor to mine and deliver such Product, Owner shall deduct the amount of such purchase or delivery from another source from the minimum purchase requirements set out in the preceding sentence.

4. PRICE

The price per ton (the "Price Per Ton") for the Product mined and delivered by Contractor to the Plant shall be the sum of the Haulage Charge, the Overburden Charge, the Miscellaneous Charge, the Profit/Overhead Charge and, if applicable, the Royalty Charge.

A. The Haulage Charge per short wet ton shall be determined from the following chart based on the number of miles the Product is hauled from the mining site to the Plant:

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<Table>
<Caption>

Distance	Haulage	Loading/ Unloading	Total
<S>	<C>	<C>	<C>
0-5 Miles	$[*]	$[*]	$[*]
5.001-10 Miles	$[*]	$[*]	$[*]

10.001-15 Miles	$[*]	$[*]	$[*]

</Table>

B. The Overburden Charge per short wet ton shall be determined from the following chart based on the ratio of the number of feet of overburden which was removed to uncover the Product as compared to the number of feet of Product:

<Table>
<Caption>
Ratio:

Overburden	Kaolin/Bauxite	Price Per Short Wet Ton
<S>	<C>	<C>
0.5	1.0	$[*]
0.75	1.0	$[*]
1.0	1.0	$[*]
1.5	1.0	$[*]
2.0	1.0	$[*]
2.5	1.0	$[*]
3.0	1.0	$[*]

</Table>

C. The Miscellaneous Charge is $[*] per short wet ton and is comprised of the following items per short wet ton:

Water Control	$[*]
Quality/Safety Management	$[*]
Motor grading/Pit Clean-Up	$[*]
Environment	$[*]
Survey Work	$[*]

TOTAL	$[*]

D. The Profit/Overhead Charge is $[*] per short wet ton.

E. Owner shall pay to Contractor the Royalty Charge per short wet ton of Product mined and delivered from Contractor's Lands to Owner which is payable by Contractor pursuant to the terms of written agreements with the landowners of the Contractor's Lands in effect on the date hereof. The Royalty Charge per short wet ton of

* Confidential Information omitted and filed separately with the Securities and Exchange Commission.

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Product mined and delivered from Contractor's Lands which are owned (not leased) by Contractor shall be $[*] per short wet ton. No Royalty Charge shall be payable to Contractor with respect to Product mined from Owner's Lands.

F. Beginning on January 1, 2003, the amount shown for Haulage Charge in subpart 4A shall be increased or decreased on each semiannual anniversary date of this Agreement to reflect any changes in the Producer Price Index ("PPI") for No. 2 Diesel Fuel (product code 2911-413) that occurred during the preceding six-month period (for an example of the calculation, see Appendix A). The adjustment shall be made as soon as the PPI for the applicable period is made available by the U.S. Department of Labor, Bureau of Labor Statistics or any other U.S. government organization that may have responsibility for publishing PPI data in the future. Contractor and Owner hereby recognize that such data is preliminary as initially published by the Bureau of Labor Statistics and agree to accept this preliminary data as final for purposes of calculating the adjustment to the Haulage Charge. Notwithstanding the adjustment determined in accordance with this subpart 4F, at no time shall the Haulage Charge be less than the amount shown for each relative distance in subpart 4A.

G. Beginning on July 1, 2003, the amounts shown for Overburden Charge and Miscellaneous Charge in subparts 4B and 4C shall be adjusted on each anniversary date of this Agreement to reflect any changes in the Producer Price Index for kaolin and ball clay (product code 1455) that occurred during the prior twelve-month period (for an example of the calculation, see Appendix A). The adjustment shall be made as soon as the PPI for the applicable period is made available by the U.S. Department of Labor, Bureau of Labor Statistics or any other U.S. government organization that may have responsibility for publishing PPI data in the future. Contractor and Owner hereby recognize that such data is preliminary as initially published by the Bureau of Labor Statistics and agree to accept this preliminary data as final for purposes of calculating the adjustment to the Overburden Charge and the Miscellaneous Charge. Notwithstanding the adjustment determined in accordance with this subpart 4G, at no time shall the Overburden Charge and Miscellaneous Charge be less than the amount shown for each charge in subparts 4B and 4C.

H. If the cost of insurance required to be carried by Contractor pursuant to Section 11 increases in any year by more than ten percent (10%) over the cost of such insurance for the immediately preceding year, Contractor shall notify Owner in writing (the Notice of Premium Increase). For a period of thirty (30) days from the date of Notice of Premium Increase, Contractor and Owner shall negotiate in good faith to reach a mutually agreeable increase in the Price Per Ton to compensate Contractor for the increased cost of insurance applicable to this Agreement. If Owner and Contractor fail to reach a mutually agreeable increase in the Price Per Ton within such thirty (30) day period, this Agreement shall terminate one year from the date of the most recent Notice of Premium Increase.

* Confidential Information omitted and filed separately with the Securities and Exchange Commission.

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5. MINING AND DELIVERY

A. Owner shall advise Contractor prior to October 1, 2003 of the tonnage of its projected 2004 Product requirements, and shall thereafter advise Contractor on or before October 1 of each year, of the tonnage of the Product it projects to require during the next calendar year. Such projections should be estimates only and Owner shall not be committed to accept deliveries of such amounts. Owner shall use reasonable efforts to advise Contractor promptly in the event of any change in its annual requirements projections for any year.

B. Owner and Contractor shall communicate regularly, and Contractor shall ensure the availability of Product for delivery hereunder on an "as needed" basis. Owner shall use its best efforts (to the extent feasible) to space evenly its actual orders of the Product, and Contractor shall be obligated to fill such orders.

C. Owner and Contractor shall jointly prepare and agree on a plan for the efficient mining of Product from the Owner's Lands and the Contractor's Lands (the "Mining Plan"). In the event of any dispute regarding the Mining Plan, the Owner shall make the final determination as to how properties will be mined.

D. Risk of loss and title for all Product mined from the Contractor's Lands shall pass to Owner upon delivery to Owner's plant in Wilkinson County, Georgia.

6. PAYMENT

Invoices for Product mined and delivered hereunder shall be sent to Owner on a monthly basis. Payment for the Product mined and delivered hereunder shall be net thirty (30) days from date of invoice.

Owner has advanced to Contractor the sum of $1,000,000 as a prepayment of Royalty Charge which shall become due for Product mined from the Contractor's Lands pursuant to this Agreement. Owner shall be entitled to credit such prepayment against Royalty Charge which would otherwise be due and shall not be required to pay any Royalty Charge until the full amount of such prepayment has been applied against the Royalty Charge otherwise payable hereunder.

7. ASCERTAINMENT OF WEIGHT

The weight of the Product delivered shall be determined by weighing on state-certified scales located at Owner's manufacturing facility in Wilkinson County, Georgia. Invoices shall include a copy of the weight-ticket covering the Product being invoiced.

8. WARRANTY

Contractor warrants that the kaolin material when delivered to the Plant will conform to all chemical and physical properties for the Product listed in Exhibit A hereto. Contractor warrants that the Product delivered hereunder shall be free of contaminants and other foreign substances rendering the Product unsuitable for the economic use of

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Owner. In the event that kaolin material delivered to Owner does not conform to all chemical and physical properties listed in Exhibit A hereto, or is contaminated with foreign substances, all such non-conforming kaolin material shall be removed by Contractor and there shall be no invoice issued by Contractor for the non-conforming kaolin material.

9. OWNER'S LANDS; RESERVED ORE & CONTRACTOR'S REPRESENTATION OF TITLE AND INDUCEMENTS TO OWNER:

A. Contractor's Lands. Contractor hereby represents that it holds title to or the right to mine crude Product located on the real property listed herein (herein called the "Contractor's Lands") which will be reserved by Contractor for sale to Owner:

Property		Tons of Product
(a)	Approximately 70 acres described on Exhibit B	2,000,000+ tons
(b)	8 acres described on Exhibit C	500,000 tons
(c)	101.6 acres described on Exhibit D	Back Up Tonnage Only
(d)	the Allen Tract described on Exhibit E.	

Contractor covenants that it has a good and marketable title, in fee simple or leasehold estate, to the Contractor's Lands, that there are no liens, mortgages or encumbrances against the same and Contractor warrants the title to all Product which Owner, its successors and assigns may remove or receive from the Contractor's Lands for processing and/or sale as against the lawful claims of all persons whomsoever. Contractor shall provide to Owner evidence, such as a current title report or title insurance commitment, of (i) Contractor's good and marketable title to the portions of the Contractor's Lands which Contractor owns in fee simple and (ii) Contractor's lessor's good and marketable title to the portions of the Contractor's Lands as to which Contractor holds a leasehold estate. Also, Contractor shall provide to Owner a copy of the lease agreement covering those portions of the Contractor's Lands as to which Contractor holds a leasehold estate and letter signed by the lessor in the form of Exhibit F attached hereto. Contractor further covenants that hereafter Contractor will not create nor permit the existence of any liens or encumbrances against the minerals or surface which will in any way adversely affect the rights of Owner hereunder. Upon any default of Contractor with respect to the covenants and warranties herein contained, it is agreed that the Owner shall have the privilege of paying-off, discharging and satisfying any such lien or encumbrance and that the amount of any such payment or payments made by Owner for such purposes, together with interest thereon at the prime rate (as published in the Wall Street Journal on the date of default declaration) plus two (2) per cent per year, may be deducted by Owner from the payments herein provided to be paid to the Contractor.

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Contractor further warrants that (a) Contractor has a good and lawful right, and full power to convey the Product on the Contractor's Lands and to authorize entry for the purposes(s) herein set forth, that the same are free from all encumbrances; (b) the Contractor's Lands connect to adjacent public roads and all present exits and entrances to the Contractor's Lands via adjacent public roads are without restriction; (c) Contractor is not a party to any litigation affecting the Contractor's Lands, the Product thereon, or Contractor's rights to sell the Product on said Contractor's Lands or any interest therein and the Contractor knows of no litigation or threatened litigation affecting the said Product and/or the Contractor's Lands; (d) Contractor has no knowledge or information of any facts or circumstances that would adversely affect the use of the Contractor's Lands for mining operations that are not set forth herein; and (e) that Contractor has not committed, except as otherwise set forth herein, nor will Contractor in the future commit, any act or acts which will encumber or cause a lien to be placed against said Product and/or the Contractor's Lands.

B. Owner's Lands

Owner holds title to or the right to mine crude Product located on the real property which is designated from time to time by Owner (herein called the "Owner's Lands") which shall be mined by Contractor pursuant to the terms of this Agreement.

Owner's Lands and Contractor's Lands are herein sometimes collectively called the "Subject Properties" or a "Property".

10. INDEMNIFICATION

To the fullest extent permitted by law, the Contractor shall indemnify and hold harmless the Owner, and agents and employees of Owner from and against claims, damages, losses and expenses, including but not limited to attorneys' fees, arising out of or resulting from performance of the Work, provided that such claim, damage, loss or expense is attributable to bodily injury, sickness, disease or death, or to injury to or destruction of tangible property (other than the Work itself) including loss of use resulting therefrom, but only to the extent caused in whole or in part by negligent acts or omissions or breach of this Agreement by the Contractor or anyone directly or indirectly employed by Contractor or anyone for whose acts Contractor may be liable, regardless of whether or not such claim, damage, loss or expense is caused in part by the negligence of a party indemnified hereunder.

11. INSURANCE

The Contractor shall purchase from and maintain in a company or companies lawfully authorized to do business in the jurisdiction in which the Subject Properties are located such insurance as will protect the Contractor and Owner from claims set forth below which may arise out of or result from the Contractor's operations under this Agreement and for which the Contractor may be legally liable, whether such operations

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be by the Contractor or by a subcontractor or by anyone directly or indirectly employed by any of them, or by anyone for whose acts any of them may be liable:

A. claims under workers' or workmen's compensation, disability benefits and other similar employee benefit acts which are applicable to the Work to be performed;

B. claims for damages because of bodily injury, occupational sickness or disease, or death of the Contractor's employees;

C. claims for damages because of bodily injury, sickness or disease, or death of any person other than the Contractor's employees;

D. claims for damages insured by usual personal injury liability coverage which are sustained (1) by a person as a result of an offense directly or indirectly related to employment of such person by the Contractor, or (2) by another person;

E. claims for damages because of injury to or destruction of tangible property, including loss of use resulting therefrom;

F. claims for damages because of bodily injury, death of a person or property damage arising out of ownership, maintenance or use of a motor vehicle; and

G. claims involving contractual liability insurance applicable to the Contractor's obligations under Paragraph 10.

The insurance required by this paragraph shall be written for not less than limits of liability specified herein or required by law, whichever coverage is greater. Coverages shall be written on an occurrence basis and shall be maintained without interruption from date of commencement of the Work until date of termination of this Agreement.

Certificates of Insurance acceptable to the Owner shall be filed with the Owner prior to commencement of the Work. These Certificates and the insurance policies required by this Paragraph 11 shall contain a provision that coverages afforded under the policies will not be canceled or allowed to expire until at least 30 days' prior written notice has been given to the Owner. Contractor shall provide evidence of continued insurance on the anniversary date of each policy of insurance.

Contractor shall maintain worker's compensation in at least the minimum amount stipulated under the Georgia worker's compensation statutes, including Employers Liability with a limit of at least:

Statutory - Georgia Benefits

Employer's Liability	$100,000 Each Accident $1,000,000 Disease - Policy Limit $1,000,000 Disease - Each Employee

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Contractor shall maintain Commercial General Liability, written on an occurrence basis, including Contractor's Liability; Independent Contractors Liability; Contractual Liability; Completed Operations and Products Liability; Personal Injury Coverage and broad form Property Damage extended to apply to completed operations; and no property damage liability exclusions pertaining to loss by explosion, collapse or underground damage.

Bodily Injury and Property Damage Liability:

General Aggregate per Project	$2,000,000
Products Completed Operations Aggregate	$2,000,000
Personal and Advertising Injury	$1,000,000
Each Occurrence	$1,000,000

Products Completed Operations shall be maintained for a minimum period of one (1) year after final payment.

Umbrella/Excess Liability:

Annual Aggregate	$5,000,000
Each Occurrence	$5,000,000

Automobile Liability including non-ownership and hired car coverage as well as owned vehicles:

Bodily Injury and Property Damage:

Combined Single Limit	$1,000,000

Contractor shall not commence Work at the Subject Properties under this Agreement until it has obtained all required insurance and until such insurance has been approved by the Owner. Approval of the insurance by the Owner shall not relieve or decrease the liability of the Contractor hereunder. Certificates of Insurance shall be filed with the Contractor prior to commencing Work.

The required insurance shall be written by a Company licensed to do business in the state in which the Subject Properties are located, at the time the policy is issued. In addition, the Company shall be acceptable to the Owner. All liability insurance policies shall name Owner additional insured, IT BEING THE INTENT THAT SUCH POLICIES AFFORD CONTRACTOR AND OWNER COVERAGE AGAINST THEIR

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NEGLIGENCE ARISING OUT OF PERFORMANCE OF THE WORK, and shall provide that coverage of Owner thereunder is primary in the event of overlapping coverage which may be carried by Owner.

The Contractor shall not cause any insurance to be canceled nor permit any insurance to lapse. All insurance policies shall include a clause to the effect that the policy shall not be canceled or reduced, restricted or limited until thirty (30) days after the Owner has received written notice. Certificates of insurance shall contain transcripts from the proper office of the insurer, evidencing in particular those insured, the extent of insurance, the location and operations in which the insurance applies, the expiration date and the above mentioned notice of cancellation clause. An acceptable Certificate of Insurance Form shall be insurance industry standard ACORD Form 27.

All insurance policies supplied by Contractor shall include a waiver of any right of subrogation of the insurers thereunder against Owner and of any right of the insurers to any set-off or counterclaim or any other deduction, whether by attachment of otherwise, in respect of any liability of any person or entity insured under any such policy.

12. FORCE MAJEURE

A. The term "Force Majeure" as used herein shall mean acts of God, natural calamities, acts of the public enemy, blockades, insurrections, strikes, slowdowns, riots, wars, disorders, civil disturbances, fires, explosions, storms, floods, landslides, washouts, labor or material shortages, boycotts, breakdowns or damage to plants, equipment or facilities, interruptions to transport, embargoes, acts of military authorities, acts of local or federal governmental agencies or regulatory bodies, court actions, arrests and constraints and, without limitation by enumeration, any other cause or causes not reasonably within the control and without the fault or negligence of the party affected which wholly or partly prevents the mining, processing, loading or transportation of Product by Contractor or the receiving, transporting, accepting or using of the Product by Owner.

B. If because of Force Majeure, either party hereto is unable to carry out its obligations under this Agreement and if such party shall promptly give to the other written notice of such Force Majeure, including a complete description thereof, then the obligation of the party giving such notice shall be suspended to the extent made necessary by Force Majeure and during its continuance; provided, however, that the party giving such notice shall use its best efforts to eliminate such Force Majeure insofar as possible with a minimum of delay. No event of Force Majeure shall relieve Owner of its obligation to make payments due for Product delivered by Contractor under this Agreement.

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13. EVENTS OF DEFAULT

In the absence of the existence of force majeure as defined in paragraph 12, if any of the following events ("Events of Default") shall occur and be continuing:

A. Any amount due hereunder, unless being disputed in good faith, shall remain unpaid for thirty (30) days after becoming due, and the party adversely affected shall have delivered a notice to the party owing such amount stating the amount due and unpaid, and the party owing (and not disputing same in good faith) shall not have paid such amount within thirty (30) days after the delivery of such notice; or

B. Contractor shall fail or refuse to provide to Owner the amount of Product as specified from time to time hereunder by Owner at the time requested by Owner; or

C. Any deliveries of kaolin materials to Owner hereunder shall fail to meet the quality specifications provided in Exhibit A; or

D. Any other covenant, obligation or agreement by either party hereunder shall not be performed or observed within twenty (20) days after written notice of the nonperformance thereof shall have been delivered to the nonperforming party by the other party; or

E. Either party shall:

(1) Fail to pay any judgment in an amount which would materially affect the net worth of such party within sixty (60) days after issuance of a writ of execution upon such final judgment;

(2) Apply for or consent to the appointment of a receiver, trustee or liquidator of such party or of all or a substantial part of its assets;

(3) Make a general assignment for the benefit of its creditors;

(4) Be adjudicated bankrupt or insolvent, or file a voluntary petition in bankruptcy;

(5) File a petition or an answer seeking reorganization under any insolvency law; or

(6) File an answer admitting the material allegations of, or consent to, or default in answering, a petition filed against it in any bankruptcy, reorganization or insolvency proceeding; or

F. An order, judgment or decree shall be entered by any court of competent jurisdiction approving a petition seeking reorganization of such party or appointing a receiver, trustee or liquidator of a party or of all or a substantial part of its assets and such order, judgment or decree shall continue unstayed and in effect for a period of thirty (30) consecutive days; or

G. Any of the representations or warranties made by a party herein shall be or become untrue in any material respect; or

H. Contractor shall be in default under any lease of any portion of the Contractor's Lands after expiration of any cure periods permitted by the lease;

then the party adversely affected by such Event of Default shall, in addition to other remedies available to such party at law or in equity, have any one (1) or more of the following remedies:

(1) The party adversely affected by such Event of Default may by written notice delivered to the other party decline to perform under this Agreement until such Event of Default shall have been cured or shall no longer exist, without relieving the defaulting party of any of its obligations hereunder;

(2) The party adversely affected by such Event of Default may, effective upon twenty (20) days' written notice to such effect delivered to the other party, terminate this Agreement without relieving the other party from any liability which shall have accrued or attached on or prior to the effective date of such termination; and/or

(3) If Contractor is in default for failure to deliver Product at the time requested or for delivering kaolin materials failing to meet quality specifications, Owner may recover all damages caused by such failure or Owner may purchase such quantities of Product from another source and Contractor shall reimburse Owner within twenty (20) days from invoice for any additional cost incurred by Owner above the Price Per Ton determined as provided herein for the Product which Contractor failed to deliver and for any costs incidental to obtaining such other supply. Termination of this Contract for any of the causes herein contained shall be without prejudice to any other right or remedy provided by this Contract or at law or in equity. Failure of either Owner or Contractor immediately to exercise its rights in any Event of Default will not constitute waiver of the injured party's rights. Both parties agree to use their best efforts to minimize the amount of damages that may be incurred as the result of an Event of Default.

14. NOTICE

All notices under this Contract required or permitted to be given by Owner to Contractor and all payments to be made by Owner to Contractor hereunder shall be delivered personally to Contractor or sent to Contractor at Contractor's address: Arcilla Mining & Land Co., P.O. Box 1371, Milledgeville, Georgia 31061, or at such other address as Contractor may hereafter furnish (by "Notice" as hereinafter described) to Owner.

All notices herein required or permitted to be given by Contractor to Owner shall be sent by registered or certified United States mail, return receipt requested, addressed to Owner at CARBO Ceramics Inc., Attn. Paul G. Vitek, 6565 MacArthur Boulevard, Suite

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1050, Irving, TX 75039, or at such other address as Owner may hereafter furnish (by "Notice" as hereinafter described) to Contractor.

15. ENTIRE AGREEMENT

This written instrument contains the entire agreement between the parties hereto concerning the subject matter hereof, and there are no other understandings or agreements between said parties or either of them in respect hereto. No change, addition to or waiver of the terms and provision hereof shall be binding upon either party unless approved in writing by an authorized representative of such party, and no modifications shall be effected by the acknowledgment or acceptance of forms containing other or different terms and conditions. This Agreement may be executed in any number of counterparts, each of which shall be deemed an original, but all of which together shall constitute a single instrument.

16. ASSIGNMENT

This Agreement shall be binding on the legal successors of the parties hereto, but shall not otherwise be assignable by either party without the written consent of the other.

17. INDEPENDENT CONTRACTOR

Contractor shall be considered an independent contractor and shall not be considered a partner, employee, agent or servant of Owner.

18. APPLICABLE LAW

This Agreement and the language used herein shall be construed and enforced in accordance with the laws of the State of Georgia.

19. MEMORANDUM OF THIS AGREEMENT

Contractor and Owner agree to execute and record in the real property records of the county where the Contractor's Lands are located a memorandum of this Agreement.

20. REPLACEMENT. This Agreement supercedes and replaces that certain Raw Materials Requirements Agreement dated November 18, 1997, between Owner and Contractor.

IN WITNESS WHEREOF, the parties hereto have caused this Agreement to be executed as of the day and year first above written.

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ARCILLA MINING & LAND CO.

By /s/ TED SMITH

Ted Smith
President & C.E.O.

CARBO CERAMICS INC.

By /s/ PAUL G. VITEK

Paul G. Vitek
Sr. Vice President, Finance & Admin.

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EXHIBIT A

RAW MATERIAL SPECIFICATION

For

WILKINSON COUNTY PLANT

Chemistry

Calcined Basis Specification(1)	%
Al2O3	[*]
SiO2	[*]
Fe2O3	[*]
TiO2	[*]
CaO	[*]
MgO	[*]
Na2O	[*]
K2O	[*]
Moisture	[*]
Grit (+325 mesh)2	[*]

Notes:

1. The average properties of blended crude clay delivered must fall within these parameters such that the target specification can be met for

ongoing plant operations using crude clay storage at the plant site.

2. Grit determined on a dry clay basis, percent of material not passing through 325 mesh screen is classified as grit. Unblundged clay in the +325 mesh sample does not count towards the grit level.

* Confidential Information in this Exhibit 10.8 has been omitted and filed separately with the Securities and Exchange Commission.

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