

United States Patent**Bullen**[15] **3,664,422**[45] **May 23, 1972**

[54] **WELL FRACTURING METHOD
EMPLOYING A LIQUIFIED GAS AND
PROPPING AGENTS ENTRAINED IN A
FLUID**

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[52] U.S. Cl.:.....**166/283, 166/308, 166/75**

[51] Int. Cl.:.....**E21b 43/26**

[58] Field of Search:.....166/308, 280, 259, 271, 281,
166/283

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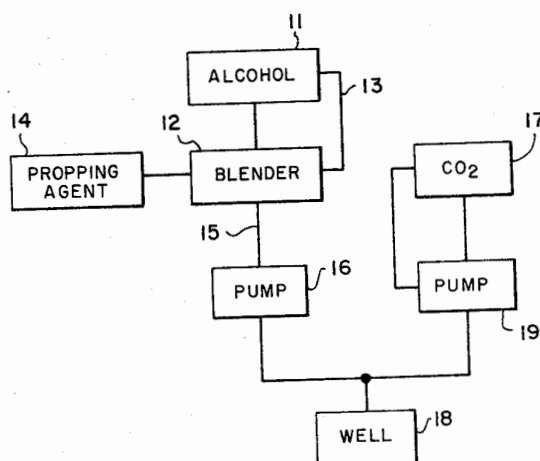
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[57]

ABSTRACT

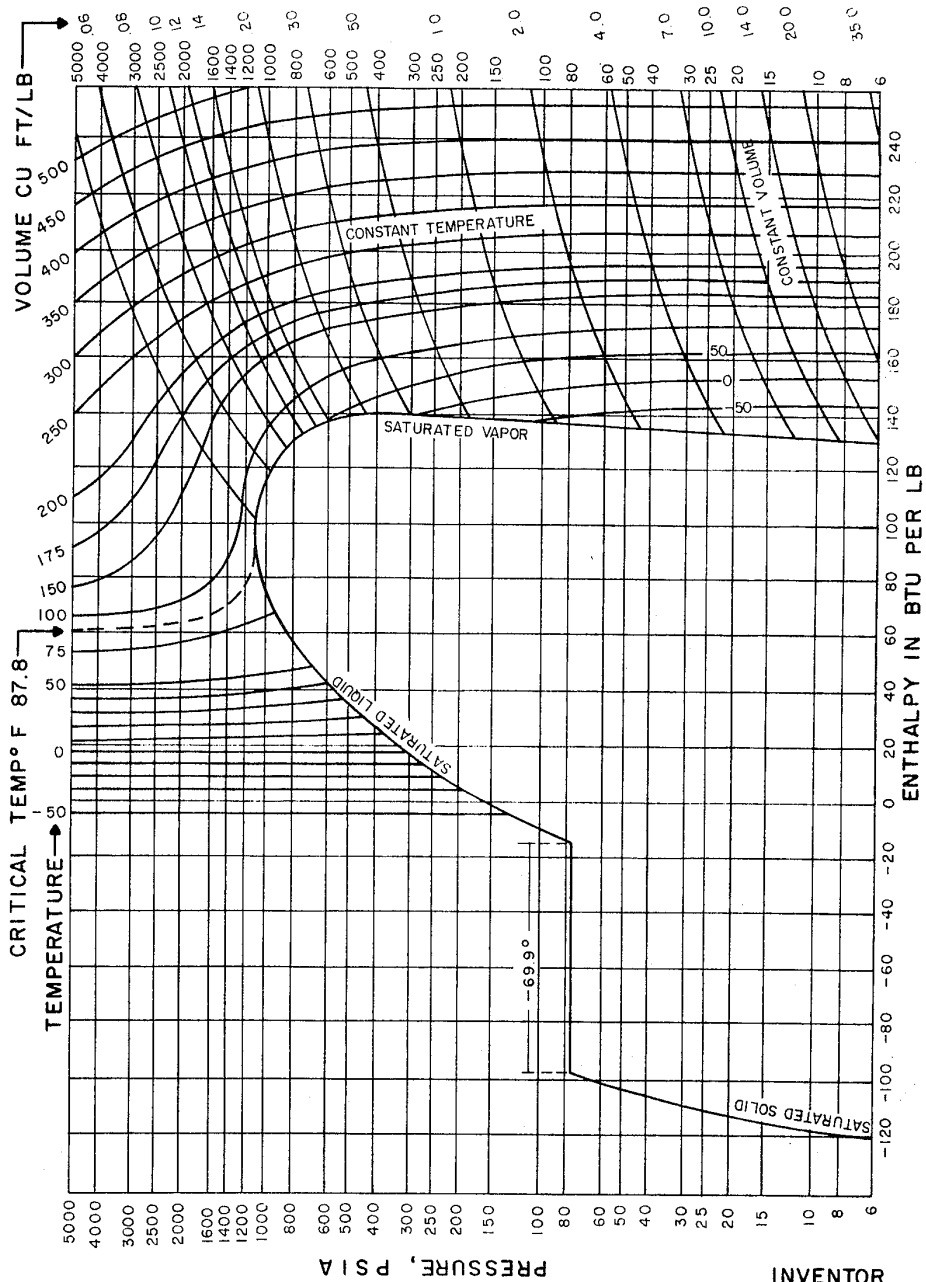
The formations surrounding a well bore are subjected to hydraulic fracturing. A liquified gas and a fluid containing entrained propping agents are injected into the formations. The liquified gas returns to its gaseous state and is therefore easily removed from the formation.

14 Claims, 6 Drawing Figures

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3,664,422

SHEET 1 OF 3



PRESSURE - TEMPERATURE - ENTHALPY CHART FOR CO₂

FIG. 1

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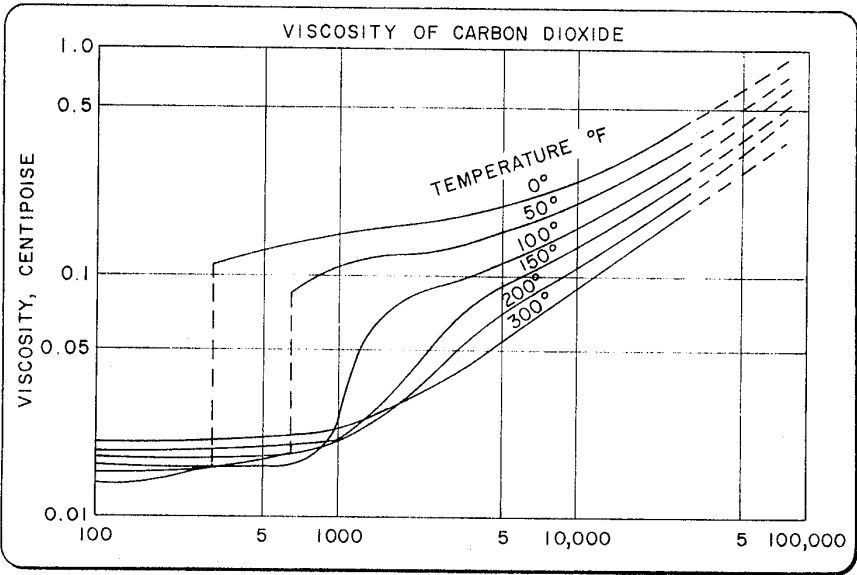


FIG. 2

THERMODYNAMIC PROPERTIES OF SATURATED CARBON DIOXIDE							
TEMPERATURE °F	PRESSURE P. S. I. A.	SPECIFIC VOLUME CONDENSED PHASE CU. FT./LB.	SPECIFIC VOLUME VAPOR CU. FT./LB.	ENTHALPY		LATENT HEAT BTU LB.	TEMPERATURE °F
				CONDENSED PHASE BTU LB.	VAPOR BTU LB.		
-69.9	75.10	.01360	1.157	-13.7	135.9	149.6	-69.9
-60	94.7	.01384	0.9270	- 9.2	136.6	145.8	-60
-50	118.2	.01409	.7492	- 4.7	137.2	141.9	-50
-40	145.8	.01437	.6113	0.0	137.8	137.8	-40
-30	177.8	.01466	.5029	4.5	138.2	133.7	-30
-20	214.9	.01498	.4168	9.1	138.5	129.4	-20
-10	257.3	.01532	.3472	13.9	138.7	124.8	-10
0	305.5	.01570	.2904	18.8	138.9	120.1	0
10	360.2	.01614	.2437	24.0	138.7	114.7	10
20	421.8	.01663	.2049	29.4	138.3	108.9	20
30	490.8	.01719	.1722	35.4	137.8	102.4	30
40	567.8	.01787	.1444	41.7	136.7	95.0	40
50	653.6	.01868	.1205	48.4	135.0	86.6	50
60	748.6	.01970	.0994	55.5	132.1	76.6	60
70	853.4	.02112	.08040	63.7	127.5	63.8	70
80	968.7	.02370	.06064	73.9	118.7	44.8	80
87.8	1069.4	.03454	.03454	97.0	97.0	0.0	87.8

FIG. 3

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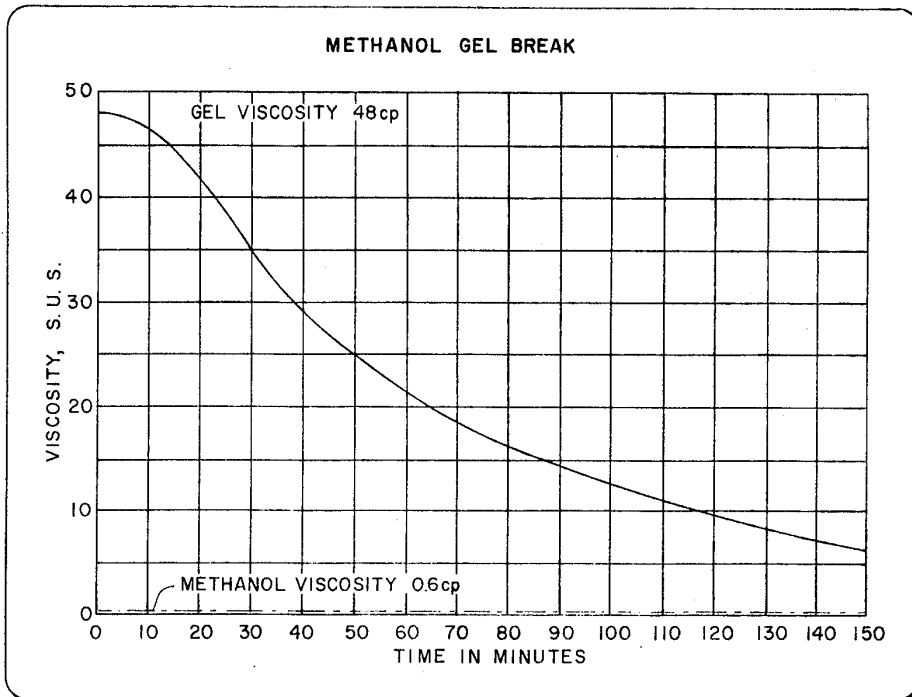


FIG. 4

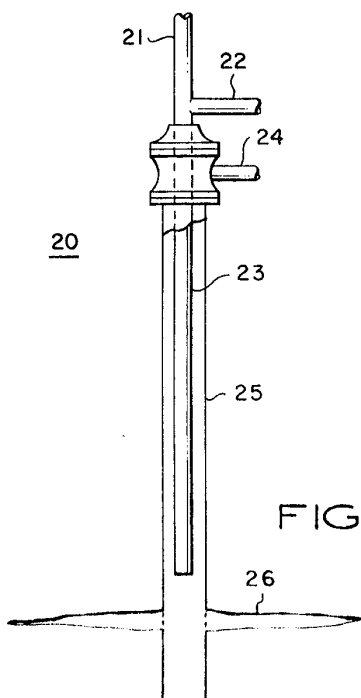


FIG. 6

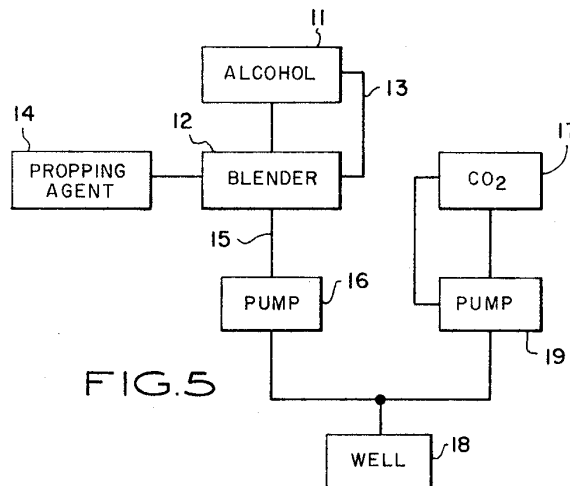


FIG. 5

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WELL FRACTURING METHOD EMPLOYING A LIQUIFIED GAS AND PROPPING AGENTS ENTRAINED IN A FLUID

BACKGROUND OF THE INVENTION

This invention relates to the art of hydraulically fracturing subterranean earth formations surrounding oil wells, gas wells, and similar bore holes. In particular, this invention relates to hydraulic fracturing utilizing a liquified gas and a fluid containing entrained propping agents.

Hydraulic fracturing has been widely used for stimulating the production of crude oil and natural gas from wells completed in reservoirs of low permeability. Methods employed normally require the injection of a fracturing fluid containing suspended propping agents into a well at a rate sufficient to open a fracture in the exposed formation. Continued pumping of fluid into the well at a high rate extends the fracture and leads to the build-up of a bed of propping agent particles between the fracture walls. These particles prevent complete closure of the fracture as the fluid subsequently leaks off into the adjacent formations and results in a permeable channel extending from the well bore into the formations. The conductivity of this channel depends upon the fracture dimensions, the size of the propping agent particles, the particle spacing, and the confining pressures.

The fluids used in hydraulic fracturing operations must have filter loss values sufficiently low to permit build-up and maintenance of the required pressures at reasonable injection rates. This normally requires that such fluids either have adequate viscosities or contain filter-loss control agents which will plug the pores in the formation. The use of fracturing fluids having relatively low viscosities in conjunction with additives which provide the low filter-loss values needed avoids excessively high friction losses in the tubing and casing. The well head pressures and hydraulic horsepower required to overcome such friction losses may otherwise be prohibitive.

Fracturing of low permeability reservoirs has always presented the problem of fluid compatibility with the formation core and formation fluids, particularly in gas wells. For example, many formations contain clays which swell when contacted by aqueous fluids causing restricted permeability, and it is not uncommon to see reduced flow through gas well cores tested with various oils.

Another problem encountered in fracturing operations is the difficulty of total recovery of the fracturing fluid. Fluids left in the reservoir rock as immobile residual fluid impede the flow of reservoir gas or fluids, to an extent that the benefit of fracturing is decreased or eliminated. The removal of the fracturing fluid may require the expenditure of a large amount of energy and time, consequently the reduction or elimination of the problem is highly desirable.

DESCRIPTION OF THE PRIOR ART

In attempting to overcome the filter-loss problem, gelled fluids prepared with water, diesel and similar low viscosity liquids have been useful. Such fluids have apparent viscosities high enough to support the propping agent particles without settling and yet low enough to give acceptable friction losses. The gelling agents also promote laminar flow under conditions where turbulent flow would otherwise take place and hence in some cases, the losses may be lower than those obtained with low viscosity-base fluids containing no additives. Certain water-soluble poly-acrylamides, oil soluble poly-isobutylene and other polymers which have little effect on viscosity when used in low concentration can be added to the ungelled fluid to achieve similar benefits.

In attempting to overcome the problem of fluid compatibility when aqueous fracturing fluids are used, chemical additives have been used such as salt or chemicals for pH control. Salts such as NaCl, KCl, or CaCl₂ have been widely used for fracturing water sensitive formations. Where hydrocarbons are used, light products such as gelled condensate have seen a wide degree of success, but are restricted in use due to the inherent hazards of pumping volatile fluids.

Low density gases such as CO₂ or N₂ have been used in attempting to overcome the problem of removing the fracturing liquid. The low density gasses are added at a calculated ratio which promotes fluid flow subsequent to the fracturing. This back flow of load fluids is usually due to reservoir pressure alone, without mechanical aid from surface, because of the reduction of hydrostatic head caused by gasifying the fluid.

SUMMARY OF THE INVENTION

The present invention provides a method of well stimulation with little or no reservoir contamination and a high percentage of load fluid recovery. A liquified gas and a fluid containing entrained propping agents are injected into the formations. Since the two aforementioned fluid phases are completely miscible they may be either blended prior to well entry, or injected separately and blended in the well. The fluids are injected until a fracture of sufficient width to produce a highly conductive channel has been formed. Particles of the propping agent, suspended in the mixture, are carried into the fracture. The injected fluid is then permitted to leak off into the formation until the fracture has closed sufficiently to hold the particles in place.

In one embodiment of the invention, liquid carbon dioxide (CO₂) and a high concentration of propping agents in a stream of gelled alcohol are simultaneously injected into the well bore. When the liquid carbon dioxide reaches the formations, it gasifies, leaving only a low fluid residual of alcohol to recover. This alcohol, in turn, is soluble in reservoir gas (methane) and is essentially returned as a vapor. The propping agents are added to a separate side stream of alcohol at atmospheric pressure and subsequently blended with the liquid carbon dioxide for injection into the well. A suitable alternate to alcohol is a light oil, condensate, or reformat (aromatic refinery by-product) gelled with additives such as aluminum stearate and time-dependant breakers.

It is therefore an object of the present invention to provide a method of fracturing the formations surrounding a well bore wherein propping agents contained in a suitable fluid are added to a liquified gas and injected into the formations.

It is a still further object of the present invention to provide a fracturing method wherein propping agents are added to a suitable fluid at atmospheric pressure and the fluid containing the propping agents is subsequently mixed with a liquified gas and injected into the formations surrounding a well bore.

It is a still further object of the present invention to provide a well fracturing method that prevents any fluid of questionable compatibility from contacting either the formation or reservoir fluids.

It is a still further object of the present invention to provide a well fracturing method that allows extension of the shut-in period of the well to an indefinite period of time for fracture healing, also allowing flow-back and evaluation at the operator's convenience.

It is a still further object of the present invention to provide a well fracturing method that includes a combination of alcohol, surface active agents and liquified carbon dioxide to be injected into the formation surrounding a well bore.

The above and other objects and advantages will become apparent from a consideration of the following detailed description when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts a pressure enthalpy chart for CO₂ in the region of interest of oil well servicing.

FIG. 2 shows the viscosity of CO₂.

FIG. 3 shows the thermodynamic properties of saturated carbon dioxide.

FIG. 4 shows the rate of reaction of gel breaker on the gelled alcohol.

FIG. 5 is a schematic representation of a system used in this invention.

FIG. 6 shows a fracturing manifold that may be used to inject the fluids into the well bore.

DETAILED DESCRIPTION OF THE INVENTION

In the preferred embodiment of the present invention liquid carbon dioxide (CO₂) is the primary fracturing fluid in a well fracturing method. Simultaneous injection of gelled alcohol (methanol) is used to carry the propping agent.

Referring now to FIG. 1, a pressure enthalpy chart for carbon dioxide in the region of interest in oil well servicing is shown. The probable path followed during a fracturing job is depicted by a "dash line." Liquid carbon dioxide is pumped from a delivery transport at approximately 300 psi and 0° F. It is pumped to an elevated pressure where it is comingled with gelled alcohol and propping agents. The temperature of the combined fluids rises due to mixing with warm fluid and as the mixed stream goes down the well, it picks up additional heat from the borehole and additional pressure due to hydrostatic head. At the perforation, pressure is at its peak and it declines after formation fracturing as fluid enters the reservoir. As the critical temperature of the carbon dioxide (87.8° F.) is exceeded, it changes to the vapor stage. When pressure is relieved at the well head after completion of the treatment, the gaseous carbon dioxide expands along a path similar to that shown, until it emerges as a gas at the well head at atmospheric pressure.

Referring now to FIG. 2, the viscosity of carbon dioxide determined by the method of "Uyehara and Watson" was calculated over the range of 0° to 300° F. for pressures from 100 to 30,000 psi. This information may be used in calculating the friction pressure drop which may be encountered when pumping pure liquid carbon dioxide into a well. The density of carbon dioxide is calculated from the equation $PV = 0.243ZTM$ where P equals pressure in psia; V equals volume in cubic feet; Z equals compressibility factor; T equals temperature in degrees Rankin; M equals weight in pounds. This equation was solved for temperatures from 0° to 200° F. and pressures from 100 psi to 10,000 psi.

Knowing viscosity and density, friction pressures of liquid carbon dioxide may then be calculated using Crittendon's correlation for pressure drop in oilfield production pipe:

$$\frac{\Delta P}{L} = \frac{518\rho^{0.79}\mu^{0.207}Q^{1.79}}{D^{4.79}}$$

where

$\Delta P/L$ = pressure drop per 1,000 feet

ρ = density, gm/cc

μ = viscosity, cp

Q = injection rate, BPM

D = pipe diameter, inches

An example of friction drop for carbon dioxide at high pressures was calculated at 15 BPM for 3.548 in. I.D. tubing at 6,000 psi indicating that the pressure drop for carbon dioxide under these conditions is only 43 percent less than that of water with 1 cp viscosity. The addition of the gelled alcohol and sand slurry to the carbon dioxide injected into a well does not appear to change the pipe friction appreciably from that calculated, although variations in perforation friction are proportionate to the increased density of the slurry according to the equation:

$$\Delta P_p = 0.323 Q^2 \rho / n^2 D^4$$

where:

P_p = perforation friction, psi

Q = injection rate, BPM

ρ = density, gm/cc

n = diameter of perforation, inches

D = diameter of perforations in inches

Orifice coefficient assumed 0.8

The thermodynamic properties of saturated carbon dioxide are shown in the Table of FIG. 3. As may be seen from this Table, the latent heat of vaporization is a function of temperature, ranging from 120.1 BTU/lb. at 0° F. (transport conditions) to 0.0 BTU/lb. at 87.8° F., when the CO₂ is entirely gaseous.

In a fracture treatment using carbon dioxide as a base fluid, the total heat absorption from the tubing, casing and formation for a stimulation incorporating 10,000 gallons of liquid

carbon dioxide would therefore be 1.0×10^6 BTU. This is usually well within the tolerable range for cooling effect corresponding to an average temperature drop throughout the system of only 20° F. to 30° F. which is quickly replaced by downhole heat transfer to equilibrium.

Under reservoir temperature and pressure conditions, the specific volume of carbon dioxide increases from that at the surface. This volume expansion increases the velocity of the fracturing fluid in the formation for improved fracture width and penetration. The volume occupied by 1,000 SCF of carbon dioxide prior to injection is 1.78 ft.³ (0° F., 300 psi). This volume expands under reservoir conditions, with the greatest effect at lower pressures.

The volume of gaseous carbon dioxide in the well reservoir at any temperature may also be calculated according to the formula:

$$V_o = 0.945 V_i \times (f)/\rho$$

where

V_o is the final volume,

V_i is the initial volume at standard conditions,

f is the compressibility factor at final conditions,

ρ is the final pressures in atmospheres.

The gelled alcohol used to carry the propping agent may be methanol or another alcohol with similar properties. Methanol is used as a proppant carrying agent in view of its compatibility with most gas and oil reservoirs, its low freezing point, and potential chemical benefits to the stimulation.

As shown in FIG. 4 the rate of reaction of gel breaker on the gelled alcohol is rapid, but allows adequate time for the displacement of the proppant into the formation at a high viscosity blend. From initial viscosity of 50 to 60 cp the gel breaks back to 2 cp as a final viscosity. By comparison, straight methanol has a viscosity of 0.6 cp. It is preferred that the alcohol be gelled to a viscosity of 20 cp or higher in order to be sufficient to carry the high concentration of propping agent through the pumping equipment and into the formation. In a low fluid residual treatment, the alcohol occupies as little as 16 percent of the total fluid volume. This alcohol is distributed over a total fracture area of many thousands of square feet, and in actual field use it is seldom recovered as a liquid.

Total recovery of the methanol without residual fluid saturation is realized by vaporization during subsequent production of the well. The saturation of alcohol in methane varies with temperature and pressure, but is generally over 250 lbs. per million cubic feet of gas under reservoir conditions.

Referring now to FIG. 5 one embodiment of a system of the present invention is shown in schematic form. An alcohol storage tank 11 is connected to a blender 12. The blender 12 may be of the type conventionally used in oil field fracturing operations and would normally include paddles, a ribbon mixer or jets for mixing and suspending propping agents in the gelled alcohol. The alcohol is gelled in this blender just prior to the addition of the propping agents. It is generally preferred to operate the blender 12 at a high speed to prevent buildup and "slugging" of the propping agent particles. A return line 13 from the blender to the alcohol storage tank 11 permits circulation to promote initial mixing of the fluid before the propping agent is added. A suitable propping agent from container 14 is added to blender 12. Discharge line 15 extends from blender 12 to high pressure fracturing pump or pumps 16. These pumps are normally positive displacement, Triplex pumps, truck mounted and specially equipped for pumping abrasive slurries at high rates and pressures.

Liquid carbon dioxide from tank or tanks 17 is injected into the well 18 by means of a pump or pumps 19. Unit 19 may be a pumping unit similar to that described in connection with pumping unit 16.

The pumps 16 and 19, blender 12, tanks 11 and 17 and other equipment are normally located some distance from the well 18 to minimize the danger in case of fire or blowout. Valves are provided throughout the system to permit control of the fluids and the disconnection of individual units of equipment as necessary.

Referring now to FIG. 6 another embodiment of the present invention is shown. A fracturing manifold particularly suited for the present invention is indicated generally at 20. The gelled alcohol with proppant enters the manifold 20 at the inlet 21. It receives the gel breaking mixture which enters at 22 and the mixture then passes down the tubing 23. The liquid carbon dioxide enters at 24 and passes down the annulus between tubing 23 and tubing 25. As the gelled alcohol including the additives exits from tubing 23 it is completely mixed with the carbon dioxide prior to entry into the formation 26.

In a typical treatment, alcohol with between 5 to 8 lbs. of proppant per gallon, depending on the well conditions, is pumped into a manifold at the rate of 7 barrels per minute. The carbon dioxide is pumped at 14 barrels per minute into the manifold and a diluted sand/liquid ratio of approximately 2 lb./gal. is injected into the well. Additional additives such as surfactants and fluid loss additives may be added to the alcohol at the blender during the treatment.

When injecting the alcohol and carbon dioxide separately into the tubing and casing, a controlled screen-out may be effected at the conclusion of the fracture treatment. Simultaneous with the flush, the annulus carbon dioxide rate is reduced to increase the bottom hole sand concentration. After the sand is displaced into the formation, the well is shut in for any length of time desired prior to the flowing back to evaluate treatment.

It is generally recognized that the stimulation benefits resulting from the present invention are two-fold:

1. highly permeable channels are developed which have the effect of allowing increased flow into the well bore; and
2. the well bore area itself is cleaned out of water blocks, mud contamination and emulsions by the scouring and flushing action of the fluids.

In the second (2) area of stimulation, the action of alcohol, carbon dioxide and surfactants would have significant benefit. It has been shown that the injection of alcohol, surfactants and carbon dioxide restores the permeability of the productive formation to gas by removing water from the capillary pores of the formation. The surfactant decreases the surface tension of the water causing a decrease in capillary pressure which allows the water to be more easily displaced by injected gas. The alcohol acts as a drying agent; thus, the combination of surfactant and dessicant forced into the formation by a gas at high pressure is very effective for removing a water block in the im-

mediate vicinity of the well bore.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of treating a subsurface earth formation penetrated by a well bore, comprising: injecting a liquified gas into the formation and injecting gelled alcohol containing entrained propping agents into said formation.
2. The method of claim 1 including the step of injecting a gel breaker into said formation.
3. The method of claim 1 wherein said gelled alcohol is gelled methanol.
4. The method of claim 1 wherein said liquified gas is carbon dioxide.
5. The method of claim 1 wherein said steps of injecting a liquified gas and said step of injecting gelled alcohol containing entrained propping agents are performed simultaneously.
6. The method of claim 1 wherein said liquified gas and gelled alcohol containing the entrained propping agents are blended prior to injection into the formations.
7. The method of claim 1 wherein said liquified gas and gelled alcohol containing the entrained propping agents are mixed after each has been injected into the well bore.
8. The method of claim 1 wherein said gelled alcohol containing the entrained propping agents is at atmospheric pressure prior to injection into the well bore.
9. The method of claim 1 wherein the entrained propping agents are sand.
10. A method of treating subsurface earth formations penetrated by a borehole, comprising: mixing propping agents with gelled alcohol, mixing said gelled alcohol containing the propping agents with a liquified gas and injecting the mixture into the formation surrounding said borehole.
11. The method of claim 10 including the step of adding a gel breaker to the gelled alcohol.
12. The method of claim 10 wherein said liquified gas is liquified N₂.
13. The method of claim 10 wherein said liquified gas is liquified CO₂.
14. A system for treating subsurface earth formations comprising:
 - means for mixing propping agents with gelled alcohol;
 - means for blending the propping agents and gelled alcohol mixture with a liquified gas; and
 - means for injecting the blend into said subsurface earth formations.

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