

Drigard & Castro

Abogados

SUPERINDUSTRIA Y COMERCIO

Radicación : 01099043 00000002

Folios: 2

Fecha (MM): 2003-12-05 17:16:47

Trámite : 002 PATENTES D 1 REGISTRO/ 530 PETICION

Residencia: 2020 DIVISION DE NUEVAS CREACIONES

AS: 85.864

Apartado 3692

Cra. 7 16-56
Bogotá - Colombia S.A.

Tel. Conm. 3802200

Tel./Fax: (57.1) 2827976
(57.1) 3802700

E.Mail:bricas@brigardycastro.com.co

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES**

E. S. D.

REF.: Expediente No. 01 099.043 solicitud de Patente a nombre de
INTEVEP, S.A.

Titulada: EMULSIÓN DE ACEITE EN AGUA COMO FLUIDO DE
FRACTURAMIENTO Y MÉTODO DE PREPARACIÓN Y APLICACIÓN

RAMIRO CASTRO DUQUE, vecino de Bogotá, portador de la tarjeta profesional No. 1003 del Consejo Superior de la Judicatura, obrando como apoderado de la Sociedad INTEVEP, S.A., según lo acredita el documento de poder presentado en la Secretaría General, de acuerdo con el Artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina, me permito solicitar que se examine si la invención contenida en la solicitud en referencia es patentable.

De acuerdo con lo anterior, me permito anexar el recibo oficial de caja No. 03-79,313 por valor de \$335.000.

Señor Superintendente,



RAMIRO CASTRO DUQUE
C.C. No. 170.322 de Bogotá
Código 340
T.P. No.1003 del C.S.J.
Cra 7 No. 16-56 Piso 9

Diciembre 05, 2003
CHP/MEV/hsr.

86

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 01-99043

EL EXTRACTO DE LA PRESENTE SOLICITUD DE PATENTE DE INVENCION FUE PUBLICADO

EN LA GACETA DE PROPIEDAD INDUSTRIAL No 529, DE FECHA 27 DE JUNIO DE 2003, EL

TERMINO HABIL SEÑALADO POR LA LEY EXPIRA EL 24 DE SEPTIEMBRE DE 2003.

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI

NO **X**

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá D.C., Enero 13 de 2006

Doctor

RAMIRO CASTRO DUQUE

Apoderado INTEVEP S.A.

ASUNTO	Radicación	01-99043	
	Trámite	002	
	Evento	001	
	Actuación	430	545
	Oficio		
	Folios	013	

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados:

- A. Para el presente estudio se tuvo en cuenta el capítulo descriptivo, comprendido en los folios 8 a 20 del expediente correspondiente a la solicitud en estudio, tal como fue radicado al inicio del trámite.
- B. Gráficos en los folios 26 y 27.
- C. El capítulo reivindicatorio tomado en cuenta para el presente estudio comprende 19 reivindicaciones y se encuentra en los folios 21 a 24, tal como fue radicado al inicio del trámite.
- D. Conforme lo establecen los artículos 9, 10 y 11 de la Decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 19 de noviembre de 2001, en el momento de la radicación se reclamó prioridad. La copia certificada de la solicitud cuya prioridad fue reivindicada (US 09/717,330 del 20 de noviembre de 2000) aparece junto con su traducción en los folios 29 a 78.

2. Objeto de la Invención:

- A. Las reivindicaciones 1 a 19 de la solicitud en estudio se refieren a: una emulsión de aceite en agua como fluido de fracturamiento que comprende: una fase dispersa de aceite y una fase continua de agua que comprende una solución de polímero entrecruzable en agua.
- B. El objeto de la solicitud se puede clasificar según la clasificación Internacional como C09K8/62.

3. Claridad de la Solicitud:

- A. El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina establece "la descripción deberá divulgar la invención de una manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"
-

Las unidades de medida en la descripción no pertenecen al Sistema Internacional de Unidades y el solicitante deberá enviar un nuevo capítulo reivindicatorio con las unidades del sistema inglés convertidas al Internacional, tal como lo establece la circular única de la Superintendencia de Industria y Comercio, título X, numeral 1.2.1.1.

De acuerdo con lo anterior, la descripción no cumple con el requisito de claridad según lo establecido en el artículo 28 de la Decisión 486.

4. Determinación del estado de la técnica:

El artículo 16 de la Decisión 486 de la Comisión establece que: "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Solo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40"

La fecha para determinar el estado de la técnica es el 20 de noviembre de 2000, tomando en cuenta la prioridad reivindicada.

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 09 K 8/62, se encontró que antes del 20 de noviembre de 2000 habían sido publicados los documentos enumerados en la siguiente tabla.

No.	Documento	Título	Fecha de publicación
D1	GB 1347721	Method of fracturing subterranean formations using oil-in-water emulsions	1974-02-27
D2	EP 0916806 A2	Method of treating subterranean formation	1999-05-19

5. Evaluación de los requisitos de patentabilidad:

El artículo 14 de la Decisión 486 de la Comunidad Andina establece que: "Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial".

En cumplimiento del artículo 14 de la Decisión 486, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad del objeto de la solicitud reivindicado en la solicitud en estudio.

A. Evaluación de la Novedad:

El artículo 16 de la decisión 486 de la Comisión de la Comunidad Andina establece:

"Una invención se considerará nueva cuando no esté comprendida en el estado de la técnica." "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

1. El documento D1 divulga un método para fracturar formaciones subterráneas en el que se emplean una emulsión que comprende una fase de hidrocarburo líquido interno y una fase acuosa externa que tiene un agente polimérico que suministra una viscosidad de por lo menos 100 centi poises (0,1 Pa s) a 70° F (21,1° C). El polímero empleado por los autores de D1, al igual que en la solicitud estudiada, es entrecruzable en agua y pueden ser gomas como las que caracterizan el objeto de la solicitud. Así, la novedad del objeto reivindicado se ve afectada por la divulgación hecha en D1.

B. Evaluación del nivel Inventivo:

El artículo 18 de la Decisión 486 de la Comisión de la Comunidad Andina dispone que: "Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

El documento D2 divulga un método para tratar una formación subterránea en el cual se emplea un líquido de fracturamiento que ha sido viscosificado a determinadas temperaturas. Como agente viscosificante se ha empleado, al igual que en la solicitud estudiada, polisacáridos, lo cual es o que caracteriza al objeto de la solicitud estudiada. El líquido de fracturamiento incluye un agente para entrecruzar el polímero empleado como viscosificante. Con esta información más la información obtenida en D1 sobre la emulsión agua – aceite y su viscosidad, un técnico medio en la materia habría derivado de manera evidente la emulsión y el método para fracturar formaciones subterráneas reivindicados por el solicitante.

Por lo tanto, la solicitud en estudio no cumple con el requisito de nivel inventivo establecido por el artículo 18 de la Decisión 486.

C. Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud podrían encontrarse afectados así:

No.	Documento	Reivindicaciones afectadas	Requisito afectado
D1	GB 1347721	1 a 19	Novedad y Nivel inventivo

No.	Documento	Relvindicaci nes afectadas	Requisito afectad
D2	EP 0916806 A2	1 a 19	Nivel inventivo

Se anexa copia de las anterioridades mencionadas.

6. Notificación

En cumplimiento del artículo 45 de la decisión 486 de la Comisión de la comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e) del capítulo quinto del título primero de la circular única No. 10 de 2001.

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 19 ENE. 2006

CONCEPTO TÉCNICO Número: 22	EXAMINADOR TÉCNICO Código: 202043
---------------------------------------	---

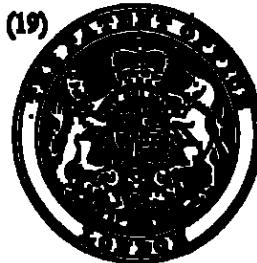
PATENT SPECIFICATION

(11) 1347721

1347721

- (21) Application No. 34162/71 (22) Filed 21 July 1971
- (31) Convention Application No. 76887 (32) Filed 30 Sept. 1970
- (31) Convention Application No. 146 349 (32) Filed 24 May 1971 in
- (33) United States of America (US)
- (44) Complete Specification published 27 Feb. 1974
- (51) International Classification E21B 43/16
- (52) Index at acceptance B1F 44
- (72) Inventor OTHAR MEADE KIEL

(19)



(54) METHOD OF FRACTURING SUBTERRANEAN FORMATIONS USING OIL-IN-WATER EMULSIONS

(71) We, ESSO PRODUCTION RESEARCH COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Houston, Texas, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of treating a well which penetrates a subterranean formation surrounding the well (which may be a gas well, a water well, an injection well or a similar borehole), employing an emulsion of the oil-in-water type.

Wells are treated with numerous fluids for various purposes, one such purpose being to increase the productivity of the well. A widely used well stimulation technique, known as hydraulic fracturing, is used to increase the productivity of a well by creating fractures in the formation surrounding the well. The hydraulic fracturing technique normally involves two basic steps: (1) injecting a fluid (the so-called "fracturing fluid") into the formation at a rate and pressure sufficient to propagate a fracture adjacent to the well and (2) placing propping agent particles in the fracture to maintain the fracture in a propped condition when the applied pressure is relieved. During the propagation step of the treatment, the fracturing fluid must have properties which provide the proper wedging effect for creating a fracture of the desired geometry. These properties relate to the fluid loss characteristic and the viscosity of the fluid employed as the fracturing medium.

It has long been known that the fluid efficiency of a fracturing fluid must be high if fractures of reasonable lengths and widths are to be obtained. Fluid efficiency, as used in fracturing operations, is defined as the percent of injected fluid which remains within the fracture and is a measure of the fluid loss characteristic of the fluid. Many fluids tend to leak off rapidly into the formation matrix and

therefore provide low fluid efficiencies. The fluid efficiency can be improved by the addition of fluid loss control additives, which are generally finely divided inert materials such as silica flour, talc, calcium carbonate, and the like.

More recently, the effect of fluid viscosity on fracture geometry has received considerable attention. It has been found that the viscosity of the fluid within a fracture plays a major role in determining the dynamic width of the fracture. Although the phenomenon is not fully understood, tests indicate that the high friction loss associated with the high viscosity fluids results in large fracture pressures which tend to force the fracture walls further apart.

Another important consideration in the design of fracturing fluid is the effect of the fluid on pumping requirements. The wedging effect described above must be achieved without excessive friction loss in the well conduit leading to the formation. High friction loss limits the available power deliverable to the formation and increases the power requirements of injection facilities.

During the proppant placement phase of the treatment, the fracturing fluid acts as a carrier for the propping agent particles. The fluid must thus be capable of suspending large concentrations of particles for long transport distances. The trend toward the use of large propping agent particles has increased the importance of the suspending properties of the fluid.

Finally, the fracturing fluid should not damage the formation. This generally means that the fluid at formation conditions must possess sufficient mobility in the formation matrix and the propped fracture to be producible into the well along with formation fluids. This operation is referred to as well clean-up.

The characteristics of an ideal fracturing fluid, then, can be summarized as follows: low friction loss in the well conduit; low fluid loss in the fracture; high friction loss in the

fracture; good proppant suspension capability; and easily produced from the formation and fracture.

As indicated above, the recent trend in fracturing fluid formulation has been toward high viscosity fluids. Experience has shown that these fluids, when properly injected, can be used to generate wide fractures of considerable length and that they are capable of suspending large propping agent particles in high concentrations. The combination of large fracture width and length and the use of large propping agent particles has resulted in unusually high fracture conductivities. Fracture conductivity is the product of the width and permeability of a propped fracture. Since well stimulation is a function of the contrast between fracture conductivity and formation permeability, fracturing treatments are normally designed to provide as high a conductivity as practicable, particularly for high permeability formations.

A variety of high viscosity fluids have been proposed for use in hydraulic fracturing operations. These fluids can be classified as oil-base or water-base fluids depending upon the composition of the continuous phase. The high viscosity oil-base fluids, typified by the gelled hydrocarbon liquids, viscous oils, and the water-in-oil emulsions, are inherently temperature sensitive and therefore lose much of their viscosity in deep, high temperature wells. Moreover, the high viscosity hydrocarbons exhibit poor mobility in tight, low permeability formations and frequently require long clean-up periods when used to fracture these formations. The viscous oil-base fluids are therefore generally not recommended for use in extremely low pressure formations, particularly those in which the pressure is less than 100 psig, because of the lack of sufficient driving force for flushing the viscous liquid from the formations.

The high viscosity water-base fluids include viscous gelled waters, gelled acids, and oil-in-water emulsions. Viscous gelled water and gelled acids owe their high viscosities to the presence of water-soluble polymers in relatively high concentrations. These gelled fluids possess good proppant suspension capabilities and because of their non-Newtonian flow behavior, can usually be pumped through the well conduit at relatively low friction loss levels. However many of these fluids have the disadvantage of being incapable of developing sufficient pressure in the fracture to create wide fractures. Moreover, in order to effect a substantial increase in fluid viscosity, the water-soluble polymers must be present at relatively high concentrations, usually between about 40 and 120 pounds per 1,000 gallons of fluid. The polymers used at these concentrations add substantially to the total cost of the operation. Laboratory tests have also shown that many of the viscous gelled waters are temperature

sensitive—they lose viscosity at high temperatures which not only reduces the pressure generated in the fracture but also increases the rate at which the fluid leaks off into the formation matrix. These two factors, i.e., low fluid viscosity and high fluid loss at high temperatures, somewhat limit dynamic fracture geometry attainable with the viscous gelled waters.

Oil-in-water emulsions have also been proposed for use in fracturing operations. In order to provide the emulsion with sufficiently high viscosities, the concentration of the oil phase in these systems must be extremely high—in the order of 95 volume percent. At these high concentrations, considerable distortion of the discrete oil particles from the usual spherical shape occurs. Such systems are difficult to handle and generally exhibit high friction loss in the well conduit. Moreover, the emulsions are difficult to stabilize. Additives such as film strengtheners, inorganic salts, and deliquescent salts have been proposed for improving the properties of the oil-in-water emulsions. However, none of the proposed oil-in-water emulsion fluids have been widely used in fracturing operations.

The present invention provides a method for treating a well which penetrates a subterranean formation which includes injecting into said well an emulsion comprising an internal liquid hydrocarbon phase, an external aqueous phase, and a surface-active emulsifying agent capable of forming an oil-in-water emulsion, said internal liquid hydrocarbon phase constituting more than 50 but not more than 80 volume percent of said emulsion, and said external aqueous phase containing a polymeric water thickening agent in a concentration sufficient to impart an apparent viscosity to said external aqueous phase of between 10 and 200 centipoises at 70°F and a shear rate of 511 reciprocal seconds.

The emulsion used in practicing the invention has a high viscosity but does not have the concomitant disadvantages associated with the high viscosity fluids of the prior art. When the method of the invention is employed for the hydraulic fracturing of a subterranean formation penetrated by the well, the emulsion is injected into the formation from the well at a pressure sufficient to open a fracture in the formation.

The friction loss characteristic of the emulsion dictates that the internal oil phase concentration be not more than 80 volume percent. Higher concentrations result in excessive friction loss when the fluid is pumped through the well conduit.

While emulsions containing up to 80 volume percent of the internal phase can be employed in the practice of the present invention, experience has shown that the stability of emulsions in the upper part of the 50 to 80 percent range is generally sensitive to the type of

70

75

80

85

90

95

100

105

110

115

120

125

130

94

mixing technique employed. In field operations, the blending equipment does not permit mixing the fluid components in precisely the desired volumetric ratios. For field application of the method, then, the concentration of the fluid components should fall within the range which is easily emulsified using field blending equipment, thus allowing for minor variations in the proportions at which the fluid components are mixed. Laboratory tests have shown that when the internal phase exceeds 75 volume percent or thereabouts, stability problems begin occurring. These tests indicated that the preferred upper limit for the internal oil phase concentration is about 75 volume percent.

The type of polymer usable in the present invention can be selected from a wide variety of organic polymers capable of giving viscous aqueous solutions or dispersions. As used herein, the term aqueous polymer solution shall mean water containing a water-dispersible or water-soluble polymer. In addition to building the fluid viscosity, the polymer also has a pronounced effect on the flow behavior of the emulsion. Many of the water-soluble or dispersible polymers behave as friction reducers when present in the external phase. This property is particularly important in fracturing operations performed in deep wells or through small diameter conduits. Polymers usable in the present invention include derivatives of cellulose, natural gums, heteropolysaccharides, polysaccharides, synthetic polymers, and blends thereof.

In practice, the volume proportion of the oil phase in the emulsion and the concentration of the polymer in the water phase will be controlled to give the desired emulsion viscosity, which preferably should be at least 100 centipoises at 70°F and 511 reciprocal seconds. Fluids having viscosities of at least 100 centipoises are capable of suspending large propping agent particles and retain sufficient viscosity at reservoir temperatures and high shear rates to provide the fluid wedges described above.

Laboratory experiments and field tests have shown that the fluid employed in the present method satisfies, unusually well, the characteristics required for a fracturing fluid. The fluids exhibited low friction loss in the well conduit, gave low fluid loss values, resulted in the generation of high pressures in the fracture, had good proppant suspension capability, and were easily removed from the formation following the fracturing treatment.

BRIEF DESCRIPTION OF THE DRAWINGS.

FIGURE 1 is a plot showing the relationship between apparent viscosity of an oil-in-water emulsion and the concentration of the internal oil phase and the concentration of a

polymeric thickening agent in the external aqueous phase.

FIGURE 2 is a plot showing the relationship between the apparent viscosity of the external water phase and the apparent viscosity of the emulsion at various concentrations of the dispersed oil phase.

FIGURE 3 is a plot showing the effect of a polymeric thickening agent on the apparent viscosity of water.

FIGURE 4 is a plot showing the effect of temperature on the apparent viscosity of various oil-in-water emulsions.

FIGURE 5 is a shear stress versus shear rate plot for an emulsion usable in the method of the present invention.

FIGURE 6 is a plot showing the relationship between apparent viscosity and the concentration of the dispersed oil phase and treating temperature for an emulsion prepared from diesel oil and an aqueous polymer solution.

FIGURE 7 is a plot similar to FIGURE 6 for emulsions prepared from a different aqueous polymer solution.

FIGURE 8 is a plot comparing the viscosity characteristics of an emulsion usable in the method of the present invention and other viscous fracturing fluids.

FIGURE 9 is a plot comparing the dynamic fluid loss behaviors of an emulsion usable in the method of the present invention and other viscous fracturing fluids.

DESCRIPTION OF THE PREFERRED EMBODIMENTS.

The fracturing method of the present invention employs an improved oil-in-water emulsion containing more than 50 but not more than 80 volume percent of an internal oil phase and the remainder an external water phase—i.e., less than 50 but not less than 20 volume percent of an external water phase. The water phase comprises an aqueous polymer solution having a viscosity of at least 10 centipoises, and preferably between 10 and 100 centipoises, at 70°F and a shear rate of 511 reciprocal seconds. The aqueous polymer solution can be prepared by adding water-soluble polymeric thickening agent to the water prior to mixing the water and oil phases together. From these fluids, the emulsion can be made by a continuous or batch mixing technique. The fracturing method is carried out by injecting the emulsion under sufficient pressure to open a fracture in the formation.

As indicated above, the external water phase of the emulsion should have a minimum apparent viscosity of 10 centipoises at 70°F and a shear rate of 511 reciprocal seconds. The viscous water retards the leak-off rate of the external phase into the formation matrix as the emulsion passes through the fracture. A rapid leak-off rate such as that provided by plain water is undesirable since it would cause

the emulsion to invert or break too readily. This would return the emulsion constituents to their original low viscosity states prematurely. The viscous water also improves the particle-carrying ability of the external phase. This becomes particularly important when a particulate fluid loss control additive is used in the system. The viscous external phase also improves the stability of the emulsion as the tendency of the dispersed oil particles to coalesce is substantially reduced.

In order to be able to suspend large propping agent particles, the fracturing fluid should have a relatively high viscosity at surface conditions. Experience has shown that the fracturing fluids used in the practice of this invention with apparent viscosities of at least 100 centipoises at 70°F and a shear rate of 500 reciprocal seconds, can adequately suspend sand particles as large as 6-8 mesh with reasonably low settling rates. These fluids can also tolerate substantial viscosity reductions at elevated formation temperatures and higher shear rates and still provide adequate fluid efficiencies for generating long, wide fractures.

In order to provide a stable emulsion in the preferred volume ratios of the oil and water phases, an emulsifier is generally required. A wide variety of emulsifiers are commercially available and include the anionic, cationic, and nonionic emulsifiers. A number of water-soluble or water-dispersible polymers also possess surface active properties and in some systems may serve as emulsifiers as well as viscosity builders.

In a typical treatment, the fracturing fluid will be formulated from four basic ingredients: an aqueous liquid providing the external water phase, a hydrocarbon liquid providing the internal oil phase, an emulsifier for promoting and stabilizing the emulsion, and a polymeric thickening agent for building viscosity of the water phase. The fracturing fluid may include other constituents such as fluid loss agents, proppants, gell breakers, water softeners, ammonium hydroxide, and demulsifiers.

Choice of the aqueous and hydrocarbon liquids will generally be governed by the availability of the liquids involved. When employing anionic or cationic emulsifiers that are sensitive to the presence of divalent ions, soft water should generally be used. However, hard water including sea water or brine, if properly treated with water-softening chemicals such as trisodium phosphate or hexametaphosphate, can be employed. If available, water from a public water supply can be used with the sensitive emulsifiers. This water, however, should be tested for hardness and softened, if necessary. As a general rule, the nonionic emulsifying agents are not sensitive to the divalent ions and therefore can be used in hard water.

The hydrocarbon liquid can be a crude oil

or a virgin or refined petroleum fraction such as kerosene, gasoline, diesel oil, gas oil, or the like. Crude oil produced from the formation to be treated is preferred because of its availability and because of its compatibility with the formation. Emulsions containing crude oil as the internal phase generally provide for rapid well clean-up following the treatment. If crude oil is not available, other hydrocarbon oils can be used. These oils preferably should have a viscosity not greater than that of formation oil. Hydrocarbon liquids having a viscosity less than 10 centipoises at formation temperature are preferred for most applications. Gas condensate, if available, can also be used and offers the advantage of promoting even more rapid well clean-up. Condensate is a light volatile liquid with an API gravity of about 50 or greater. It normally comprises the condensable hydrocarbon fractions produced from a gas or a gas condensate well. The major portion of these fractions generally include C_7 - C_{10} hydrocarbons. In the reservoir, the condensable hydrocarbon fractions, or at least a portion thereof, are in the gaseous state but at surface conditions they condense to form a liquid which is separated from the gas and collected in suitable surface facilities. The condensate constituting the internal phase of the emulsion will retain its liquid character as long as the fracturing pressure is maintained on the emulsion. However, when the applied pressure is removed and the well is placed on production, the dispersed condensate particles in the fracture will be vaporized as formation gas commingles with the emulsion or emulsion phase. Vaporization of the condensate not only breaks the emulsion but transforms the oil phase of the fracturing fluid into a highly mobile gas. This permits rapid well clean-up, particularly for gas or condensate wells.

The selection of the most efficient emulsifier and its concentration in the water phase will depend upon several factors, including the composition of the oil and water to be emulsified, the temperature of the formation to be treated, the type of blending equipment available, and the composition of the additives to be employed in the emulsion. The most efficient emulsifier or blend of emulsifiers for a particular system may require a selection by a trial-and-error process. The trial-and-error selection can be aided and guided by the familiar hydrophile-lipophile-balance (HLB) method. Emulsifiers or blends of emulsifiers having HLB numbers in the range from 8 to 18 are generally considered oil-in-water emulsifiers.

As indicated earlier, the emulsifier may be an anionic, cationic, or nonionic surfactant. Suitable anionic emulsifiers for many emulsions of the invention include the alkali, amine, and other carboxylic acid soaps. As is well known in the emulsion art, these soaps are generally the salts of long-chain fatty acids derived from

70

75

80

85

90

95

100

105

110

115

120

125

130

naturally-occurring animal and vegetable fats and oils. The mixed fatty acids of tallow, coconut oil, palm oil, soybean oil, and the like are the most commonly employed. Other sources of carboxylic acids include tall oil and rosin. Many of the carboxylic acid soaps such as the alkali and amine soaps have the added advantage in the system contemplated of being deactivated in the presence of divalent ions. When the emulsion comes in contact with formation fluids, the calcium or magnesium ions, which are almost always present in the connate water, deactivate the emulsifier and break the emulsion. This returns the oil and water components to their original demulsified viscosities which are much lower than the emulsion viscosity. When the well is placed on production, the water and oil are then easily flushed from the formation.

When using the alkali and amine soaps, it is usually advisable to operate with soft water because these soaps are sensitive to divalent ions such as calcium. The water available at the well site generally will require treatment with a water-softening chemical as suggested earlier. These soaps are generally made by adding the fatty acid and a base to the water phase prior to blending the two phases together. Alternatively, the fatty acid can be dissolved in the oil phase and the base in the water phase. The soap forms at the interface as the two phases are brought together. Suitable bases for the preparation of alkali soaps include sodium hydroxide and potassium hydroxide. Suitable bases for forming the amine soap can be selected from a wide variety of amines such as triethanolamine, morpholine, and 2 - amino - 2 - methyl - 1,3-propanediol.

Ammonium hydroxide when added in small concentrations to the oil phase of systems described above appears to improve the stability of the emulsion. Laboratory experiments and field tests have shown that when the water phase containing an emulsifier and the oil phase containing the ammonium hydroxide are brought together, a more stable emulsion is formed than in the same system without the ammonium hydroxide. The concentration of the ammonium hydroxide can be from 0.01 to 0.10 volume percent based on the volume of the oil, with about 0.05 volume percent being preferred.

Although the cationic emulsifying agents are not widely used for promoting oil-in-water emulsions, some exhibit high HRL numbers indicating that they can be employed for this service. The cationic emulsifying agents of principal importance are amines and quaternary ammonium salts such as polyoxyethylene sorbitol oleate-polyoxyethylene amine blend, polyoxyethylene alkyl amine, and quaternary ammonium derivatives.

The nonionic emulsifying agents are generally independent of water hardness and pH and

are therefore compatible with hard water. A few of the general purpose nonionic emulsifiers capable of promoting stable oil-in-water emulsions include polyoxyethylene sorbitan monolaurate, polyoxyethylene lauryl ether, polyoxyethylene monooleate, polyoxyethylene octylpropylene stearate, polyoxyethylene cetyl ether, polyoxyethylene sorbitan esters of mixed fatty and resin acids, polyoxyethylene glycol monopalmitate, and polyoxyethylene sorbitan monopalmitate.

The concentration of the emulsifying agent in the water will depend upon a multitude of factors. The optimum concentration for a particular system will generally be determined on a trial-and-error basis. Concentrations between 0.1 weight percent and 3.0 weight percent of the emulsifying agent based on the weight of the aqueous phase should be satisfactory for most applications.

As mentioned previously, many of the polymeric thickening agents which possess surface active properties can be used as the emulsifier to promote the oil-in-water emulsion. The carboxyvinyl polymers are representative of this group. Polyvinylcarboxylic acid neutralized with a long-chain amine and a common base such as sodium hydroxide is capable of promoting extremely stable oil-in-water emulsions. The emulsified system exhibits excellent temperature resistance and therefore can be used in deep, high-temperature wells.

The polymeric thickening agent can be any one of a variety of long-chain, water-soluble polymers capable of building the viscosity of an aqueous solution. These polymers are commonly referred to as gums and include the acrylic polymers such as polyacrylamide and polyacrylic acid; the vinyl polymers such as polyvinylpyrrolidone and polyvinylcarboxylic acid neutralized with a long-chain amine and a common base; and the cellulose derivatives such as sodium carboxymethylcellulose, sodium carboxymethylhydroxyethylcellulose, methylcellulose, hydroxyethylcellulose, and ethylhydroxycellulose.

Natural gums include guar gum, gum arabic, gum tragacanth, gum karaya, and the like. Also usable are the microbial fermentation gums such as dextran and the heteropolysaccharides produced by the bacteria of the genus *Xanthomonas*. In some applications, it may be desirable to use both natural and synthetic polymers, since their respective chemical effects on the emulsion may be different. For example, many of the natural gums operate to form protective colloids on the dispersed oil particles, as well as thickening the water phase of the emulsion. Many of the natural gums also are more effective in controlling the fluid loss of the fluid than are the synthetic polymers. In selecting the polymeric thickening agent and the emulsifying agent for a particular system, care should be exercised to insure that the chemicals are compatible.

elevated temperatures than are viscous gelled water or viscous oil base fluids. The three plots presented in FIGURE 8 illustrate the effect of temperature on fluid viscosity for three different fluids. The viscous gelled water consisted of tap water containing about 0.96 weight percent of a cross-linked guar gum. The viscous oil was an asphaltic oil having a viscosity of 1,000 centipoises at 150°F. The emulsion contained 70 volume percent of a 2 centipoise oil and 30 volume percent of tap water containing 0.43 weight percent of polyacrylamide and 0.14 weight percent of guar gum. A nonionic emulsifier was also used in this system. The viscosity and temperature relationship for each of the fluids was measured on a Model 50B Fann Viscometer. As illustrated in FIGURE 8, the viscosity for the emulsion fluid exhibited very little viscosity reduction below about 250°F, whereas the viscous gelled water and viscous oil fluids exhibited substantial reductions in viscosity throughout the temperature range investigated. From these data, it is evident that the emulsion fluid retained substantially more viscosity at high temperatures and therefore would be expected to generate longer and wider fractures than either the viscous gelled water or the viscous oil base fluids at temperatures above about 180°F.

Dynamic fluid loss tests using the same fluids also revealed that the emulsion fluid provided better fluid loss control than either the viscous gelled water or the viscous oil fluids. The emulsion and viscous gelled water contained the equivalent of 20 pounds per 1,000 gallons of fluid of a particulate fluid loss additive. The fluid loss additive used in the water base fluids was a blend of silica flour and a commercial additive. The viscous oil contained the equivalent of 30 pounds per 1,000 gallons of fluid of a commercial fluid loss additive. Briefly, the fluid loss tests were performed on 2 millidarcy Bandera sandstone cores saturated with salt water. A differential pressure of 950 psi was maintained across the core during each test. The amount of fluid passing through the core was collected in a graduated cylinder and the total volume was recorded for a 20 minute test period. The fluid loss test for the viscous gelled water and the emulsion were run at temperatures of 150°F, 200°F, and 250°F. For the viscous oil fluid, the fluid loss tests were run at 110°F, 150°F, and 190°F. The relatively flat curve for the emulsion fluid indicates that the temperature effect on fluid loss of the emulsion was slight. For the other two fluids, however, increasing temperature resulted in substantial increases in fluid loss. The reason for the improved performance of the emulsion fluids is not fully understood. It appears, however, that the ability of the emulsions to retain higher viscosities at elevated temperatures partially accounts for the improved fluid loss results.

Another factor which undoubtedly plays an important role in the mechanisms involved relates to the composition of the fluids. In the emulsion containing a major volume proportion of an internal phase and a minor volume proportion of an external phase, the two-phase flow of fluid through the core would be expected to be less than the flow of a single-phase fluid.

From the data appearing in Figures 8 and 9, it can be concluded that the emulsion fluid will provide higher fluid efficiencies in generating a fracture in a subterranean formation than would the other two types of fluids investigated.

The viscosity-temperature relationship for the emulsions is further illustrated in the plots of FIGURE 4 which were prepared from recorded laboratory data. The viscosities of the three emulsion samples were measured at various temperatures. The three emulsion samples had the following compositions:

Sample 1:

Tap water : 350 milliliters
Kerosene : 815 milliliters
Polyacrylamide : 1.6 grams
25% aqueous solution polyacrylic acid : 1 milliliter
Long-chain diamine : 0.5 milliliter

Sample 2:

Tap water : 350 milliliters
Kerosene : 1400 milliliters
Tall oil acid : 1.4 milliliters
Sodium hydroxide : 0.2 grams
Hydroxyethylcellulose : 1.6 grams
Guar gum : 0.8 grams

Sample 3:

Tap water : 350 milliliters
Kerosene : 815 milliliters
Tall oil acid : 1.4 milliliters
Sodium hydroxide : 0.2 grams

The viscosities of the samples were measured on a Fann Model 39 Viscometer at temperatures ranging from 80°F to 200°F for samples 2 and 3 and from 80°F to 280°F for sample 1. FIGURE 4 illustrates the relationship between emulsion viscosity at a shear rate of 511 reciprocal seconds and emulsion temperature. The emulsion containing the polyacrylamide polymer (sample 1) showed no loss in apparent viscosity in the temperature range investigated. Thus, a fluid having the formulation of sample 1 can be used to fracture a formation having a normal subsurface temperature of 280°F based on its viscosity at 80°F. The viscosity of sample 2 containing the hydroxyethylcellulose and the guar gum declined from about 800 centipoises to about 400 centipoises between temperatures of about 80°F and about 200°F. The viscosity of the emulsion without polymer declined from 24 centipoises to 8

98
100

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) EP 0 916 806 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
19.05.1999 Bulletin 1999/20

(51) Int Cl.® E21B 43/26

(21) Application number: 98308720.7

(22) Date of filing: 26.10.1998

(84) Designated Contracting States: AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE Designated Extension States: AL LT LV MK RO SI (30) Priority: 05.11.1997 US 884534 (71) Applicant: Halliburton Energy Services, Inc. Duncan, Oklahoma 73536 (US) (72) Inventors: • Shuehart, Chris E. Norman, Oklahoma 73072 (US)	• Terraena, John M. Duncan, Oklahoma 73533 (US) • Stabaugh, Billy F. Marlow, Oklahoma 73055 (US) • McCabe, Michael A. Duncan, Oklahoma 73533 (US) (74) Representative: Wain, Christopher Paul et al A.A. THORNTON & CO. Northumberland House 303-306 High Holborn London WC1V 7LE (GB)
--	--

(54)

Method of treating subterranean formation

(57) A subterranean formation is treated with a viscosified aqueous well treating composition which breaks into a thin fluid at temperatures in the range 100°F to 300°F. A breaker system is included in the compositions comprised of an alkali metal chlorite or hypochlorite breaker and a breaker activator comprised of copper II ion or an amine, or both.

EP 0 916 806 A2

99

EP 0 916 806 A2

Description

[0001] The present invention relates to a method of treating a subterranean formation, and more particularly, but not exclusively to a method involving breaking fracturing fluids utilized in the stimulation of subterranean formations.

[0002] It is common practice to treat subterranean formations to increase the permeability or conductivity of such formations by procedures which are identified generally as fracturing processes. For example, it is a conventional practice to hydraulically fracture a well in order to produce one or more cracks or "fractures" in the surrounding formation by mechanical breakdown of the formation. Fracturing may be carried out in wells which are completed in subterranean formations for virtually any purpose. The usual candidates for fracturing, or other stimulation procedures, are production wells completed in oil and/or gas containing formations. However, injection wells used in secondary or tertiary recovery operations, for example, for the injection of water or gas, may also be fractured in order to facilitate the injection of fluids into such subterranean formations.

[0003] Hydraulic fracturing is accomplished by injecting a hydraulic fracturing fluid into the well and applying sufficient pressure on the fracturing fluid to cause the formation to break down with the attendant production of one or more fractures. The fracture or fractures may be horizontal or vertical, with the latter usually predominating, and with the tendency toward vertical fracture orientation increasing with the depth of the formation being fractured. Usually a gel, an emulsion or a foam having a proppant such as sand or other particulate material suspended therein is introduced into the fractures. The proppant is deposited in the fractures and functions to hold the fractures open after the pressure is released and the fracturing fluid flows back into the well. The fracturing fluid has a sufficiently high viscosity to retain the proppant in suspension or at least to reduce the tendency of the proppant to settle out of the fracturing fluid as the fracturing fluid flows along the created fracture. Generally, a viscoifier such as a polysaccharide gelling agent is used to gel the fracturing fluid to provide the high viscosity needed to realize the maximum benefits from the fracturing process.

[0004] After the high viscosity fracturing fluid has been pumped into the formation and fracturing of the formation has occurred, it is desirable to remove the fluid from the formation to allow hydrocarbon production through the new fractures. Generally, the removal of the highly viscous fracturing fluid is realized by "breaking" the gel or in other words, by converting the fracturing fluid into a low viscosity fluid. Breaking the gelled fracturing fluid has commonly been accomplished by adding a "breaker," that is, a viscosity-reducing agent, to the fracturing fluid prior to pumping into the subterranean formation. However, this technique can be unreliable and sometimes results in incomplete breaking of the fluid, particularly when gel stabilizers are present, and/or premature breaking of the fluid before the fracturing process is complete.

[0005] U.S. Patent No. 5,413,178 discloses a means for breaking an aqueous based fracturing fluid or treatment fluid at a temperature above 200°F, through use of an effective amount of an alkali metal chlorite or hypochlorite. The breaker is particularly effective in the temperature range of 200°F to about 300°F. It has been determined that alkali metal chlorites generally are ineffective as a breaker within a reasonable time period at temperatures below about 200°F.

[0006] Thus, it is desirable to provide means by which alkali metal chlorites or hypochlorites can be utilized to provide controlled breaks of viscosified fluids at temperatures in the range of from about 100°F to about 200°F.

SUMMARY OF THE INVENTION

[0007] We have now devised a method of controllably breaking an aqueous fracturing fluid or treatment fluid which has been viscosified with a polysaccharide at temperatures in the range of from about 100°F to about 300°F. The method is basically comprised of the addition of an effective amount of copper II ion or an amine, or both, to the fracturing or treatment fluid in combination with an effective amount of an alkali metal chlorite or hypochlorite breaker whereby the breaker is activated to provide a controlled break at the above mentioned temperatures.

[0008] The invention provides a method of treating a zone of a subterranean formation penetrated by a well bore, the static temperature of the zone being above about 100°F (38°C), which method comprises injecting into the well bore and into contact with said formation an aqueous gelled fluid comprised of an aqueous liquid, a viscosity increasing amount of a gelling agent comprising a galactomannan, a modified or derivatized galactomannan or a cellulose derivative or any mixture of two or more thereof, a breaker comprising an alkali metal chlorite or hypochlorite or any mixture of two or more thereof, present in an amount sufficient to effect a controlled reduction in the viscosity of said fluid, and a breaker activator comprised of copper II ion or an amine or any mixture of two or more thereof, present in an amount sufficient to activate said breaker.

[0009] The viscosifying or gelling agent employed in the present invention includes natural and derivatized polysaccharides which are soluble, dispersible or swellable in an aqueous liquid to yield viscosity to the liquid. One group, for example, of polysaccharides which are suitable for use in the present invention includes arabic gum, ghatti gum, karaya gum, tamarind gum, tragacanth gum, guar gum, locust bean gum and the like. Modified gums such as carboxyalkyl

102
100

EP 0 916 806 A2

derivatives, like carboxymethyl guar, and hydroxyalkyl derivatives, like hydroxypropyl guar can also be employed. Doubly derivatized gums such as carboxymethylhydroxypropyl guar (CMHPG) can also be used.

[0010] Modified celluloses and derivatives thereof can also be employed in the practice of the present invention, for example, cellulose ethers, esters and the like. In general, any of the water-soluble cellulose ethers can be used. Those cellulose ethers include, among others, the various carboxyalkyl cellulose ethers, such as carboxyethyl cellulose and carboxymethyl cellulose (CMC); mixed ethers such as carboxyalkyl ethers, e.g., carboxymethyl hydroxyethyl cellulose (CMHEC); hydroxyalkyl celluloses such as hydroxyethyl cellulose (HEC) and hydroxypropyl cellulose; alkylhydroxyalkyl celluloses such as methylhydroxypropyl cellulose; alkyl celluloses such as methyl cellulose, ethyl cellulose and propyl cellulose; alkylcarboxyalkyl celluloses such as ethylcarboxymethyl cellulose; alkylalkyl celluloses such as methylethyl-cellulose; hydroxyalkylalkyl celluloses such as hydroxypropylmethyl cellulose; and the like. A preferred derivatized cellulose is a hydroxyethyl cellulose grafted with vinyl phosphonic acid such as disclosed in U.S. Patent No. 5,087,585, to which reference should be made for further details. The most preferred polysaccharides are the galactomannans, modified or derivative galactomannans, and cellulose derivatives, examples of which are given above.

[0011] The chemistry and materials involved in the preparation of polysaccharide gelled fluids of the type described above (often referred to as "Linear Gels") is well understood in the art. Typically, the amount of gelling or viscosifying agent employed in the aqueous gel depends upon the desired viscosity of the aqueous gel. The gelling agent generally is present in an amount of from about 10 to about 120 pounds per 1000 gallons of fluid. The preferred concentration is in the range of from about 15 to about 60 pounds per 1000 gallons of fluid.

[0012] The aqueous gel may include a cross-linking agent to further enhance the development of viscosity by cross-linking the gelling agent. The cross-linking agent can comprise a borate releasing compound or any of the well known transition metal ions which are capable of creating a cross-linked structure with the particular gelling agent utilized. Examples of such cross-linking agents include a borate releasing compound such as sodium tetraborate, aluminum, zirconium or titanium chelates, antimony compounds and the like. The cross-linking agent can be controlled to permit introduction of the aqueous gel into a well bore before the viscosity of the gel significantly increases.

[0013] The aqueous fluid utilized in the preparation of the gel often includes a salt such as potassium chloride to minimize the swelling of clays and the chances of damage to the subterranean formation upon contact with the fluid. The aqueous fluid may include any of the other conventional additives such as proppants, pH control agents, bactericides, clay stabilizers, surfactants and the like which do not adversely react with the other constituents to inhibit performance of the desired treatment upon a subterranean formation.

[0014] The breaker system for the gelled fluid of this invention comprises an effective amount of at least one compound selected from the group consisting of alkali metal chlorites or hypochlorites in at least partially water soluble form and an effective amount of a breaker activator comprised of copper II (Cu^{2+}) ion or an amine, or both copper II ion and an amine. When the activator includes both copper II ion and an amine, a synergistic effect takes place which causes a faster reduction in viscosity than when copper II ion alone or an amine alone are used.

[0015] The amount of breaker system employed is that amount required to reduce the viscosity of the stabilized gelled fluid at a temperature above about 100°F to a preselected lower viscosity or to a complete break within a desired period of time. The optimum or effective amount of breaker system employed in the present invention depends on factors such as the injection period desired, the particular gelling agent and its concentration, the particular breaker and the formation temperature as well as other factors. Typically, however, from about 0.1 to about 30 pounds of the chlorite breaker is employed per 1000 gallons of gelled fluid. Most preferably, to achieve a desired break in from about 8 to 24 hours in the fluid, from about 1 to about 10 pounds of chlorite is employed per 1000 gallons of fluid.

[0016] The amount of breaker activator employed, comprised of copper II ion alone, an amine alone or both copper II ion and an amine, is that amount required to activate the chlorite breaker in the temperature range of from about 100°F to about 300°F to yield a lower viscosity within a desired period of time. The optimum or effective amount of activator depends on factors such as the injection period desired, the particular gelling agent and its concentration, the particular breaker and the formation temperature as well as other factors.

[0017] When copper II ion is used, it can be added to the gelled fluid in various forms such as salts, e.g., copper chloride, copper sulfate and the like, aqueous solutions of such salts or an aqueous solution of a complex formed by a chelating agent such as ethylenediaminetetraacetic acid (EDTA) and copper II ion. Typically, in whatever form the copper II ion breaker activator takes, it is combined with the gelled fluid in an amount whereby the copper II ion is present in the gelled fluid in an amount in the range of from about 3 to about 240 parts per million (ppm). Preferably, the copper II ion is present in the fluid in an amount in the range of from about 9 to about 90 ppm so that the fluid breaks in less than about 24 hours at temperatures below about 200°F.

[0018] Alternatively, as mentioned above, an amine can be substituted for the copper II ion as the activator. A variety of amines can be used including, but not limited to, tetraethylenepentamine, butyl amine, ethylene diamine and diethylene triamine as well as ammonia and ammonium salts such as ethylene diamine hydrogen chloride salt. Of these, diethylene triamine is preferred. Typically, the amine is combined with the gelled fluid in an amount in the range of from about 0.025 to about 40 pounds of amine per 1000 gallons of fluid. Most preferably, to achieve desired breaks in less