(12) UK Patent Application (19) GB (11) 2 383 355 (13) A

(43) Date of A Publication **25.06.2003**

(21) Application No **0130880.8**

(22) Date of Filing **22.12.2001**

(71) Applicant(s)
Schlumberger Holdings Limited
(Incorporated in the British Virgin Islands)
PO Box 71, Craigmuir Chambers,
Road Town, Tortola, British Virgin Islands

(72) Inventor(s)
Isabelle Couillet
Trevor Hughes

(74) Agent and/or Address for Service
Christophe Macquet
Schlumberger Cambridge Research Limited,
Intellectual Property Law Department,
High Cross, Madingley Road, CAMBRIDGE,
CB3 0EL, United Kingdom

(51) INT CL^7
E21B 43/26 , C09K 7/02 , E21B 33/138

(52) UK CL (Edition V)
E1F FGP FPA FPC

(56) Documents Cited

WO 1987/001758 A1	**US 6194356 B**
US 5566760 A	**US 4432881 A**
US 4266610 A	**US 20010020531 A1**

(58) Field of Search
UK CL (Edition T) **E1F** FGP FMB FMC FPA FPC
INT CL^7 **C09K** 7/02, **E21B** 33/138 43/22 43/26
Other: **Online: WPI, EPODOC, PAJ**

(54) Abstract Title
An aqueous viscoelastic fluid containing hydrophobically modified polymer and viscoelastic surfactant

(57) An aqueous viscoelastic fluid for use in the recovery of hydrocarbons comprises a viscoelastic surfactant and a hydrophobically-modified polymer. The surfactant concentration and/or the hydrophobically-modified polymer concentration in said fluid is below their / its overlap concentration. The polymer has principal backbone, with pendant hydrophobic groups grafted onto it. The fluid may further comprise a salt. The surfactant is preferably ionic and forms worm-like, thread-like or rod-like micelles in aqueous solution. The hydrophobically modified polymer has a molecular weight between 10,000 and 10,000,000 g/mol, preferably between 100,000 and 1,000,000 g/mol. The fluid may be used as a drilling fluid, a completion fluid, a work over fluid, a packer fluid, a conformance or permeability control fluid and, more particularly, a fracturing fluid. The fluid is capable of forming a gel able to be broken down on contact or mixing with hydrocarbons, without forming an emulsion. The worm-like micelles of the gel degrade to spherical micelles when the gel is broken by hydrocarbon. The fluid leak off-rate into the formation rocks is lower than the leak-off rate of a pure viscoelastic surfactant of equivalent rheology.

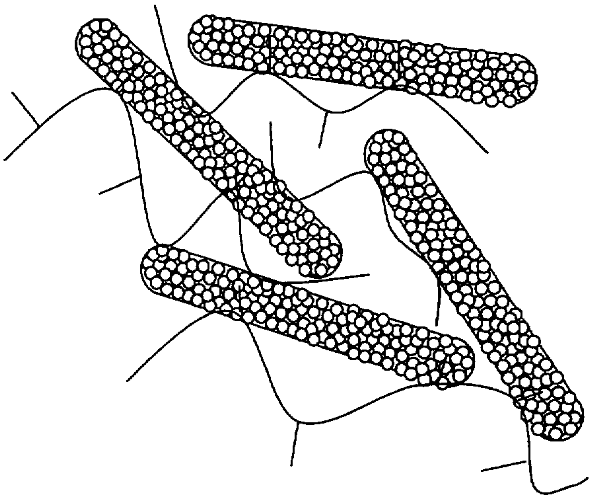


Fig. 1

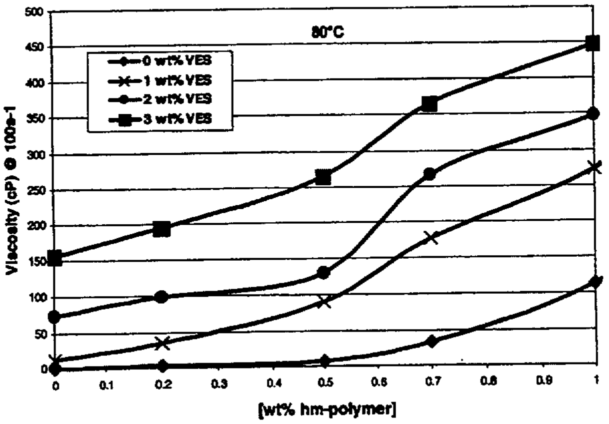


Fig. 2

GB 2 383 355

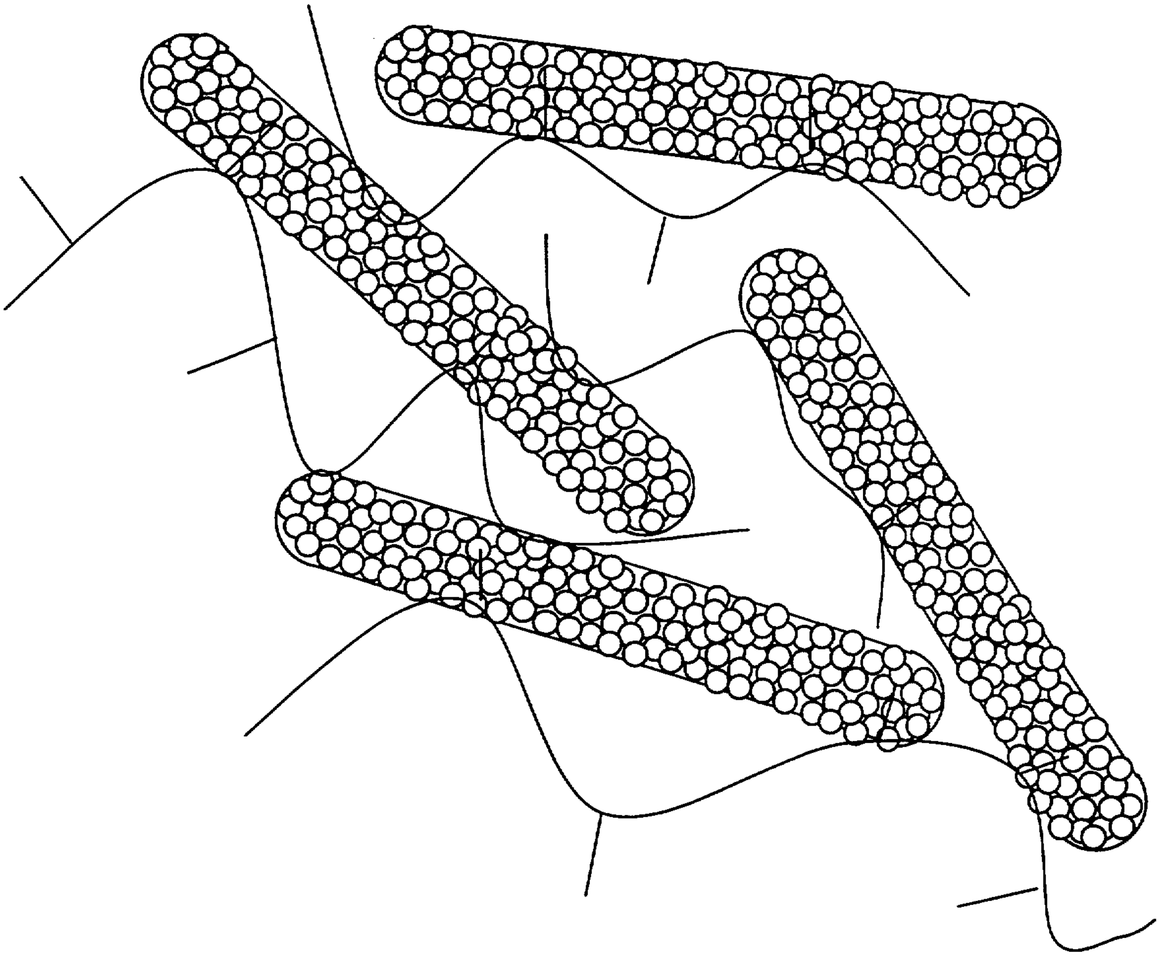


Fig. 1

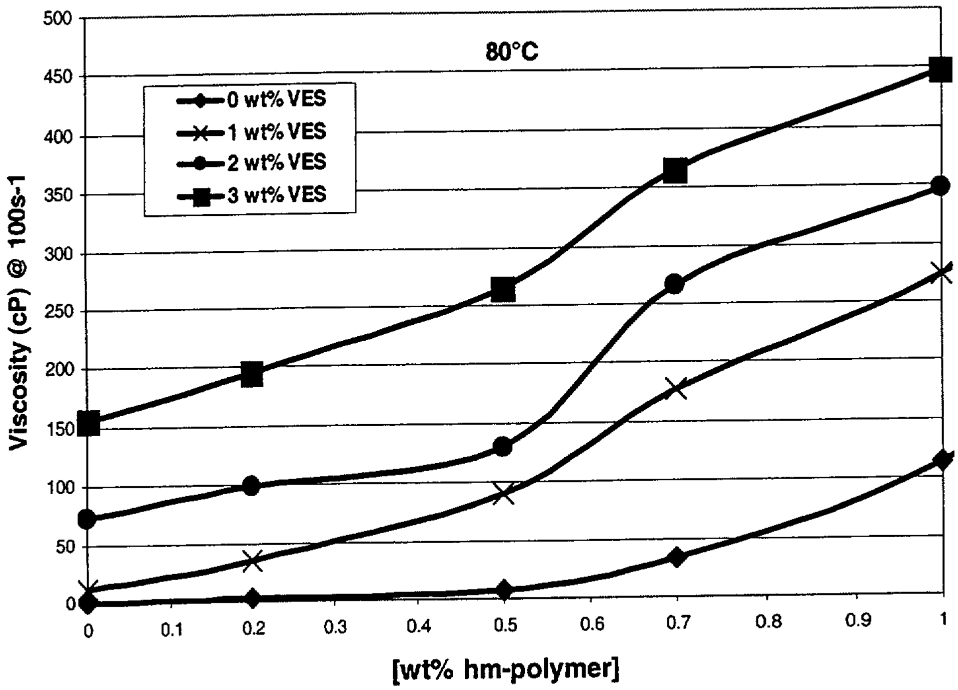

80°C
0 wt% VES
1 wt% VES
2 wt% VES
3 wt% VES
Viscosity (cP) @ 100s-1
500
450
400
350
300
250
200
150
100
50
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
[wt% hm-polymer]

Fig. 2

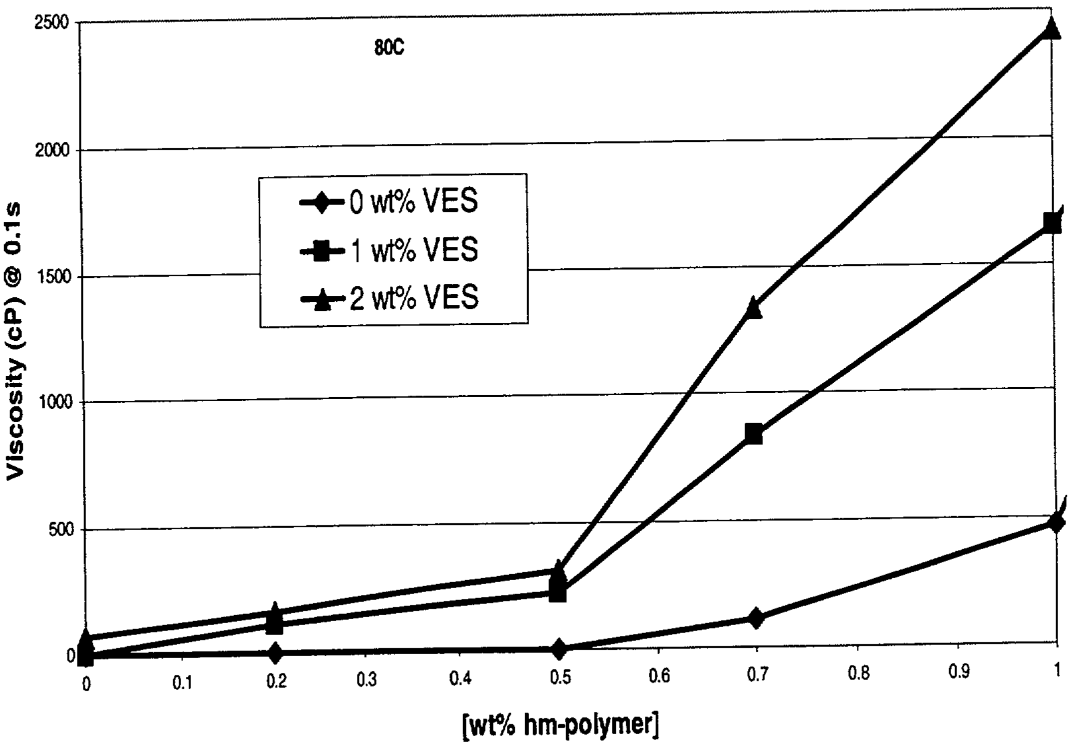

80C
0 wt% VES
1 wt% VES
2 wt% VES
Viscosity (cP) @ 0.1s
2500
2000
1500
1000
500
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
[wt% hm-polymer]

Fig. 3

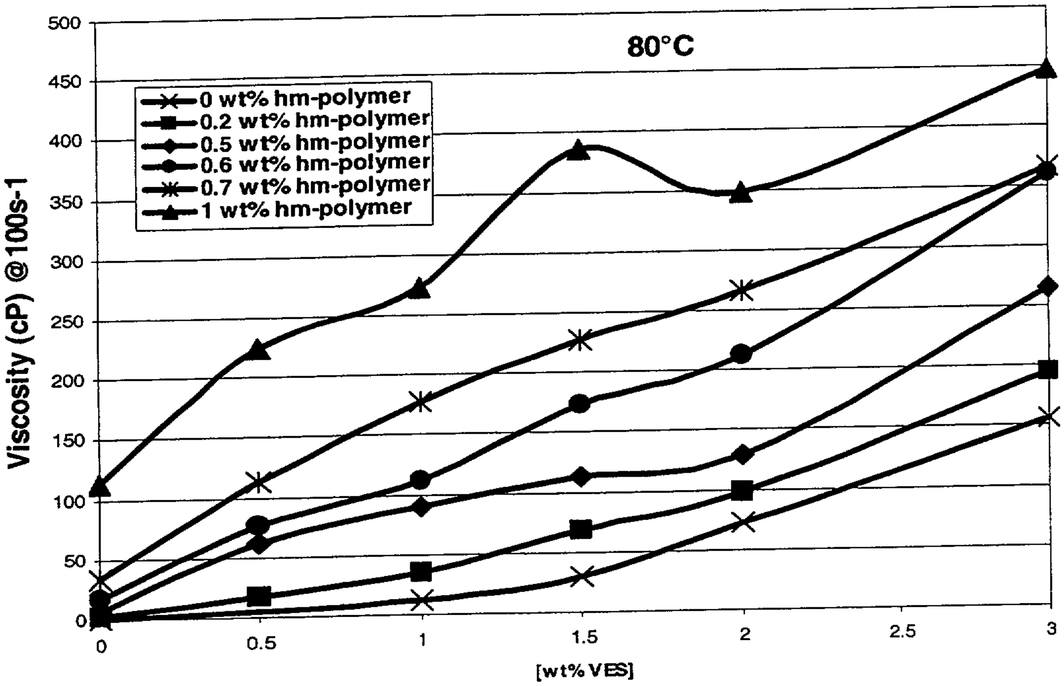

80°C
0 wt% hm-polymer
0.2 wt% hm-polymer
0.5 wt% hm-polymer
0.6 wt% hm-polymer
0.7 wt% hm-polymer
1 wt% hm-polymer
Viscosity (cP) @100s-1
500
450
400
350
300
250
200
150
100
50
0
0
0.5
1
1.5
2
2.5
3
[wt% VES]

Fig.4

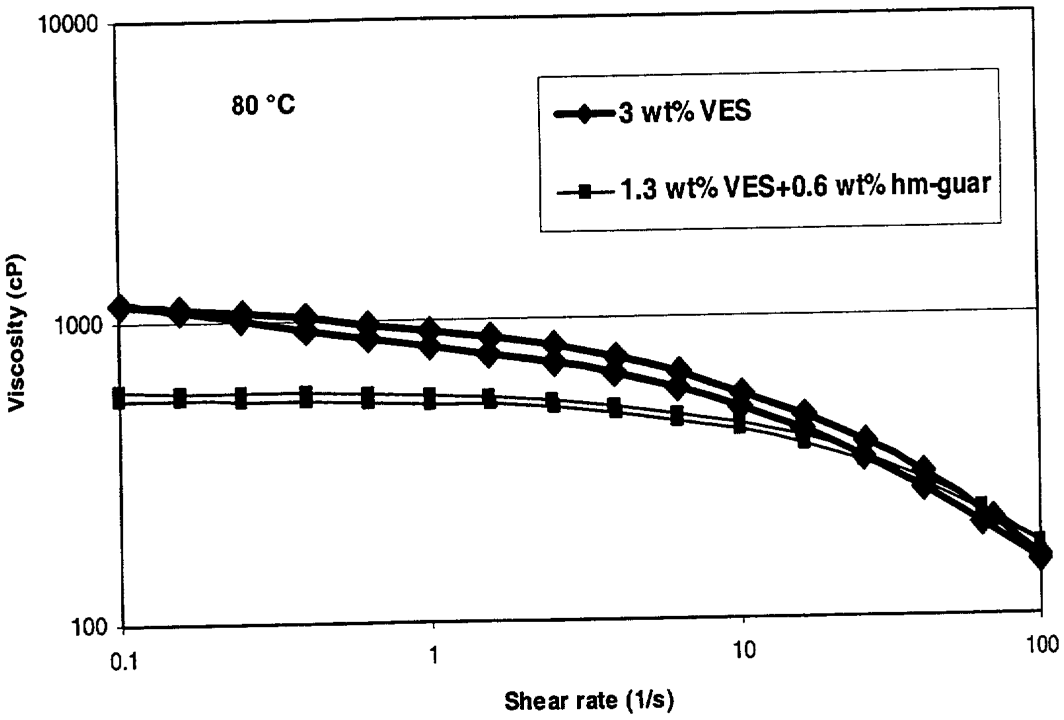

80 °C
3 wt% VES
1.3 wt% VES+0.6 wt% hm-guar
Viscosity (cP)
10000
1000
100
0.1
1
10
100
Shear rate (1/s)

Fig. 5

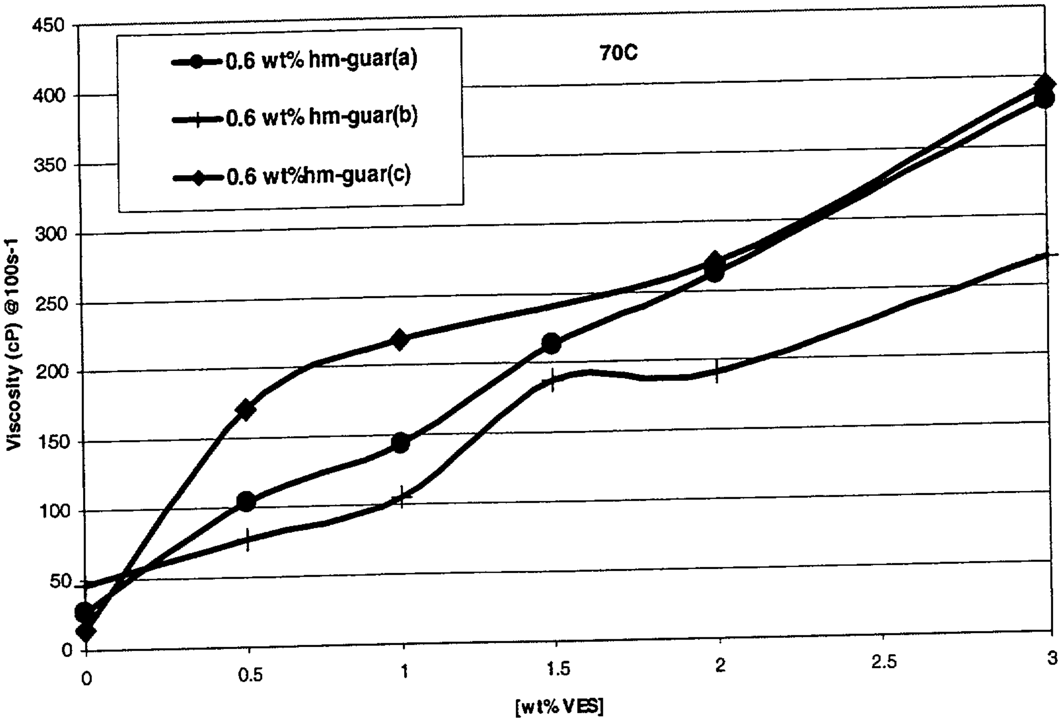

70C
0.6 wt% hm-guar(a)
0.6 wt% hm-guar(b)
0.6 wt%hm-guar(c)
Viscosity (cP) @100s-1
450
400
350
300
250
200
150
100
50
0
0
0.5
1
1.5
2
2.5
3
[wt% VES]

Fig. 6

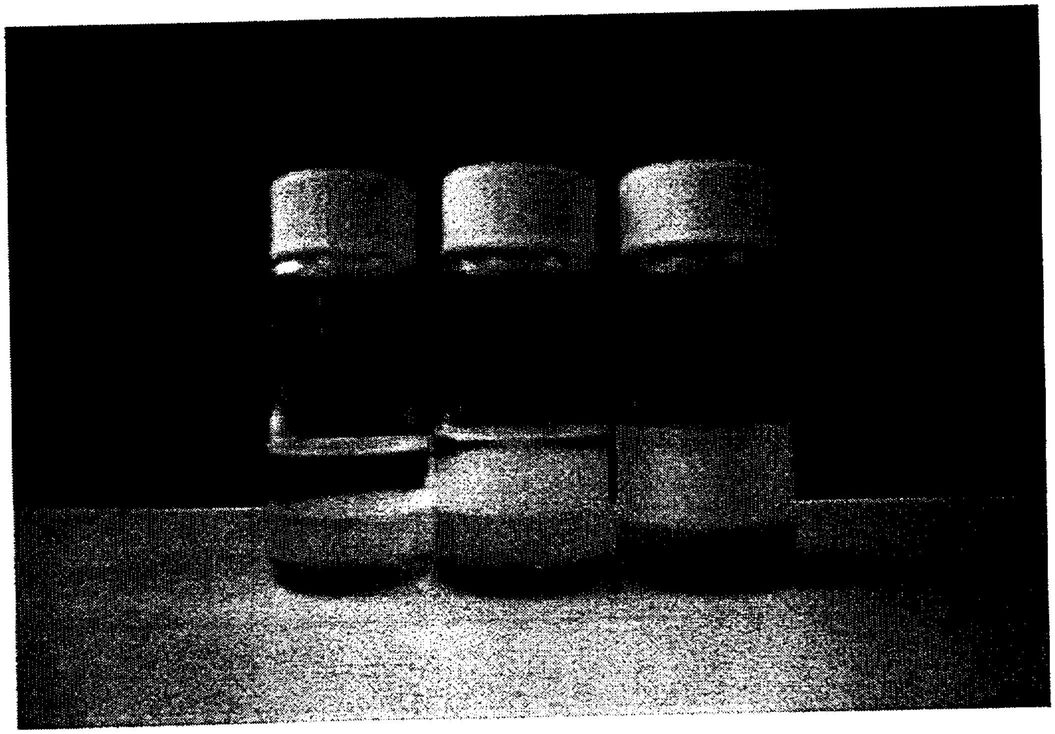


Fig. 7

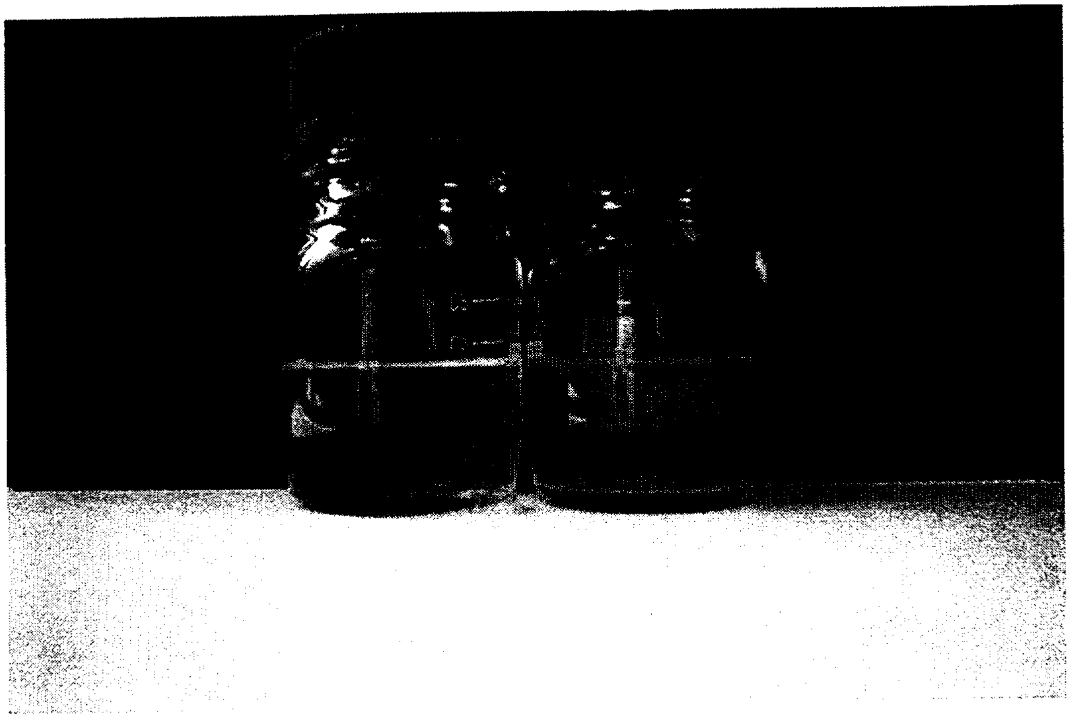


Fig. 8

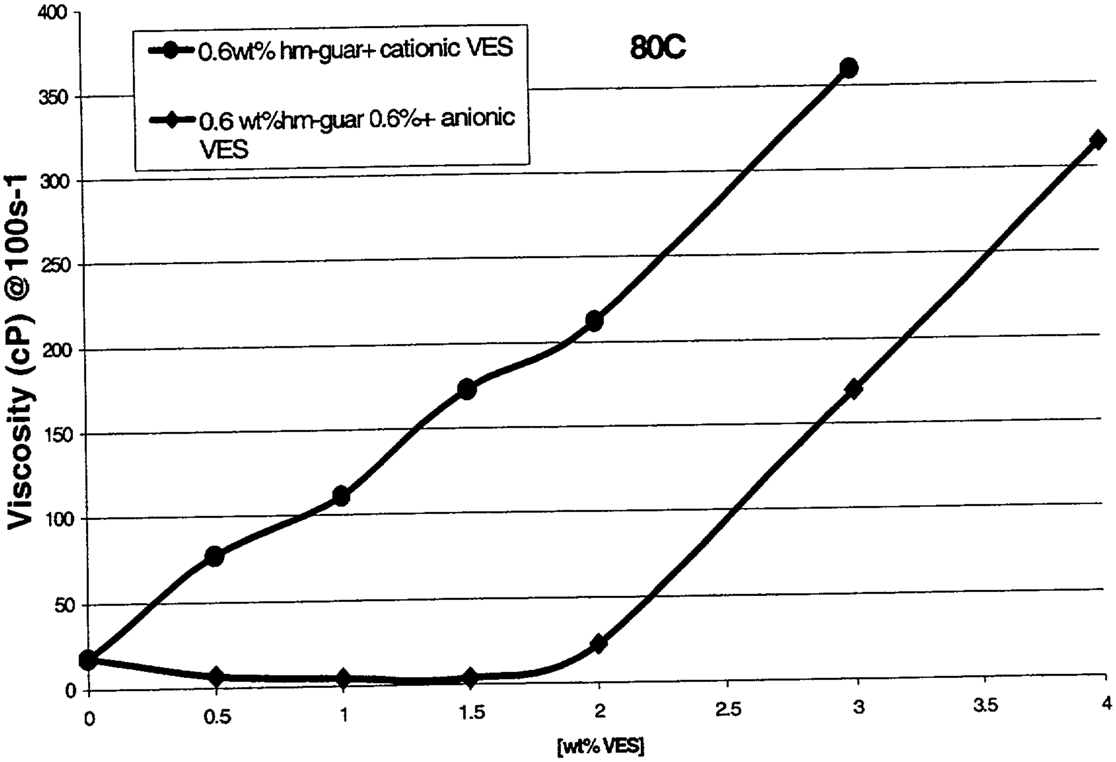
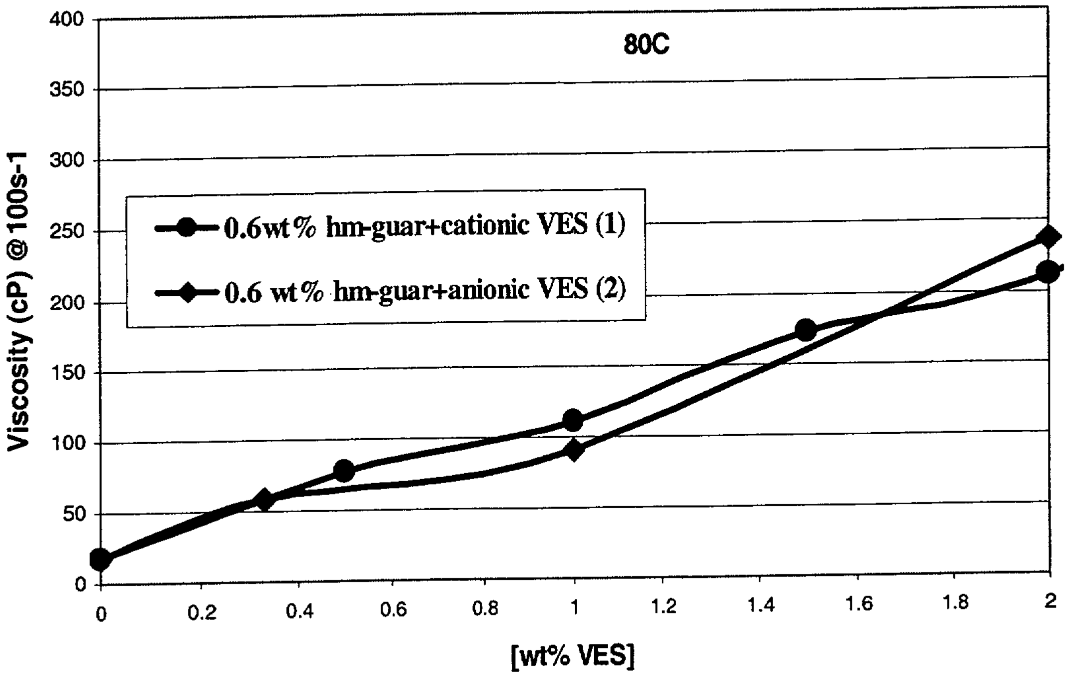
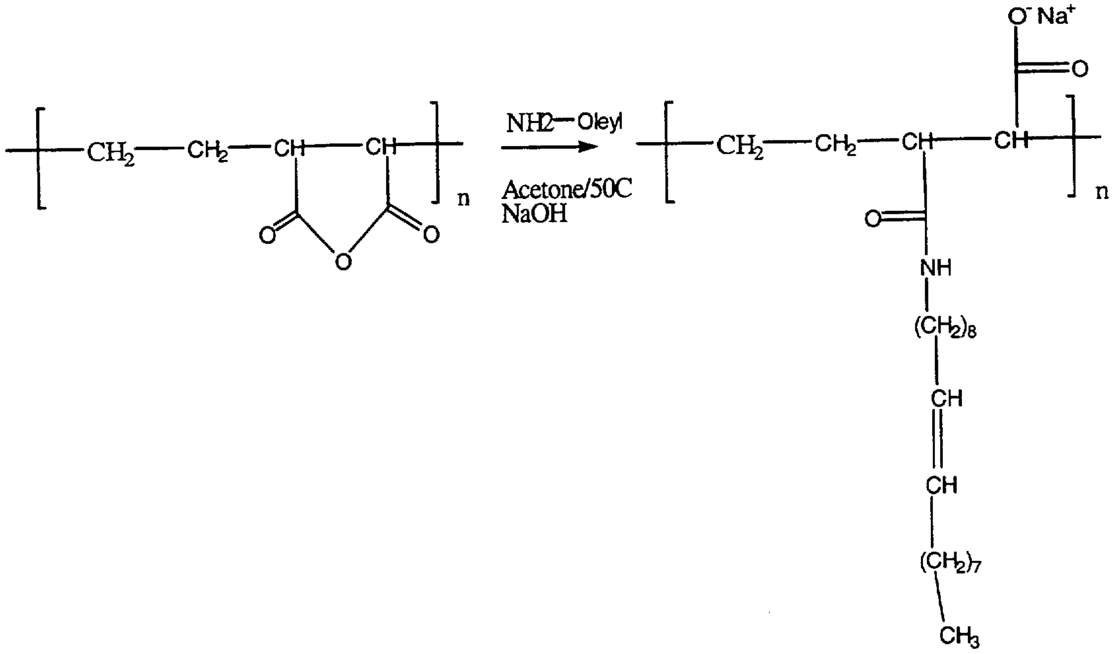

400
350
300
250
200
150
100
50
0
Viscosity (cP) @100s-1
0
0.5
1
1.5
2
2.5
3
3.5
4
[wt% VES]
80C
0.6wt% hm-guar+ cationic VES
0.6 wt%hm-guar 0.6%+ anionic VES

Fig. 9



80C
Viscosity (cP) @100s-1
[wt% VES]
0.6wt% hm-guar+cationic VES (1)
0.6 wt% hm-guar+anionic VES (2)
0
50
100
150
200
250
300
350
400
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2

Fig. 10



CH2
CH2
CH
CH
O
O
O
n
NH2—Oleyl
Acetone/50C
NaOH
O⁻ Na⁺
O
O
NH
(CH2)8
CH
CH
(CH2)7
CH3

Fig. 11

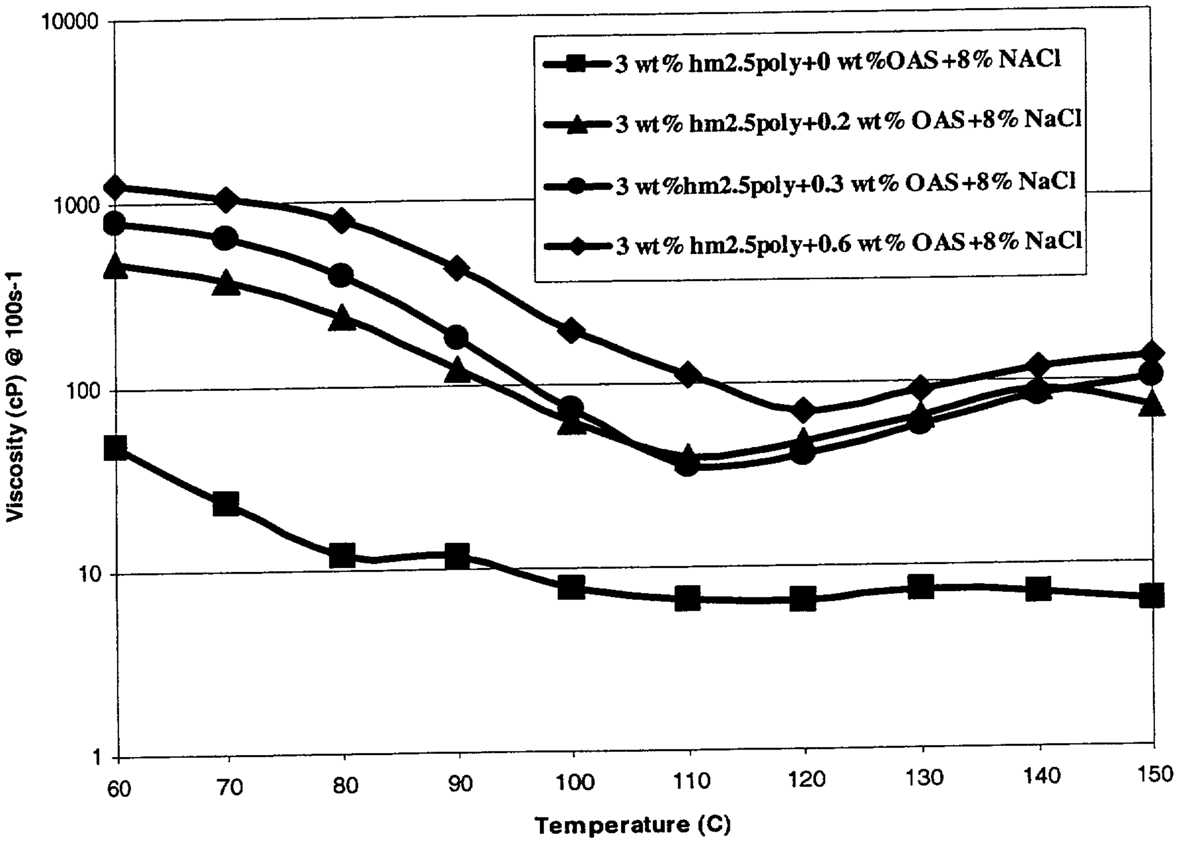

10000
1000
100
10
1
Viscosity (cP) @ 100s-1
60
70
80
90
100
110
120
130
140
150
Temperature (C)
■ 3 wt% hm2.5poly+0 wt%OAS+8% NACl
▲ 3 wt% hm2.5poly+0.2 wt% OAS+8% NaCl
● 3 wt%hm2.5poly+0.3 wt% OAS+8% NaCl
◆ 3 wt% hm2.5poly+0.6 wt% OAS+8% NaCl

Fig. 12

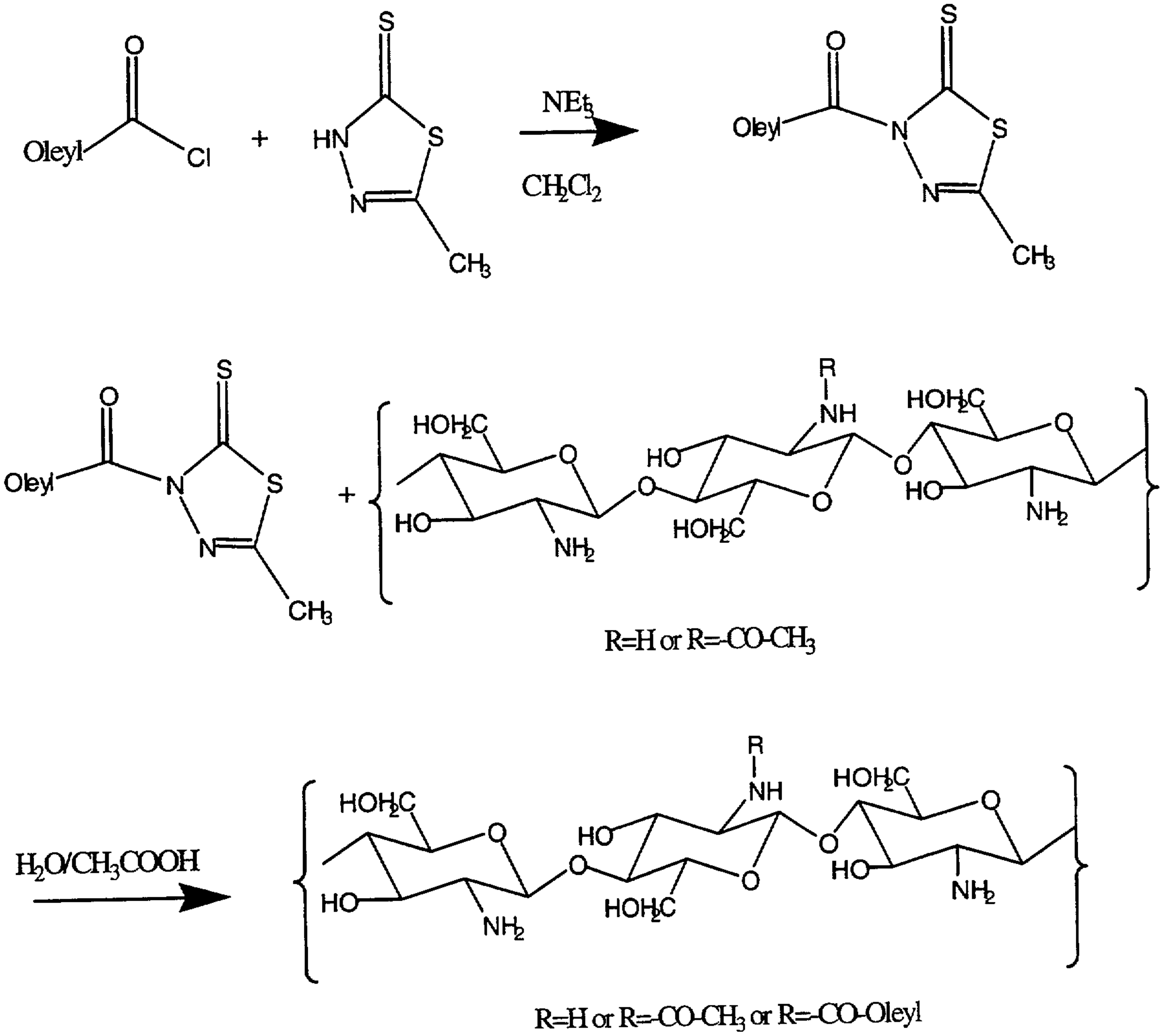

Oleyl
O
Cl
+
S
HN
N
CH3
NEt3
CH2Cl2
R
NH
HOH2C
HO
O
NH2
R=H or R=-CO-CH3
H2O/CH3COOH
R=H or R=-CO-CH3 or R=-CO-Oleyl

Fig. 13

Aqueous Viscoelastic Fluid

The present invention concerns an aqueous viscoelastic fluid comprising a surfactant and a hydrophobically-modified polymer for use in the recovery of hydrocarbons and, in particular, for use as a fracturing fluid.

BACKGROUND OF THE INVENTION

Hydrocarbons, such as oil or natural gas, are obtained from hydrocarbon-bearing subterranean geologic formations by drilling a wellbore that provides a partial flow path allowing said hydrocarbons to reach the surface. Hydrocarbons migrate via flow paths connecting a reservoir within the formation and the wellbore.

However, impeded flow paths may lead to an insufficient hydrocarbon production. In such case, various techniques are used to stimulate the hydrocarbon production. Amongst these techniques, it is common to inject specialised fluids via the wellbore into the formation at sufficient pressures to create fractures in the formation rocks. Thereby, channels are created through which the hydrocarbons may more readily flow into the wellbore. The latter technique is referred to as fracturing or hydraulic fracturing and the specialised fluids used in said technique are referred to fracturing fluids.

Ideally, fracturing fluids should impart a minimal pressure drop in the pipe within the wellbore during placement and have an adequate viscosity to carry proppant material that prevents the fracture from closing. Moreover, said fracturing fluids should have a minimal leak-off rate to avoid fluid migration into the formation rocks so that, notably, the fracture can be created and propagated and should degrade so as not to leave residual material that may prevent accurate hydrocarbons to flow into the wellbore.

PRIOR ART

Early fracturing fluids were constituted of viscous or gelled oil but, with the understanding that formation damage due to water may not be as important as originally thought, aqueous fracturing fluids mainly consisting of "linear" polymeric gels comprising guar or hydroxyethyl cellulose were introduced. In order to attain a sufficient fluid viscosity and thermal stability in high temperature reservoirs, linear polymer gels were partially replaced by cross-linked polymer gels such as those based on guar crosslinked with borate or polymers crosslinked with metallic ions. However, as it became apparent that crosslinked polymer gel residues might deteriorate the permeability of hydrocarbon bearing formations, fluids with a lower polymer content and foamed fluids were introduced. In addition, some additives were introduced to improve the clean-up of polymer-based fracturing fluids. These included polymer breakers.

Nevertheless, this is only with polymer-free fracturing fluids comprising viscoelastic surfactants that minimal formation damages was attained. These fluids are disclosed, notably, in the patents published under the numbers US-4,695,389, US-4,725,372 and US-5,551,516. One well-known polymer-free aqueous fracturing fluid comprising a viscoelastic surfactant, which has been commercialised by the company group Schlumberger under the trademark ClearFRAC ™, is a mixture of a quaternary ammonium salt, the N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride, with isopropanol and brine, said brine including 3 % by weight of ammonium chloride and 4 % by weight of potassium chloride. The viscoelastic surfactant molecules, present at a sufficient concentration, aggregate into overlapping worm- or rod-like micelles, which confer the necessary viscosity to the fluid to carry the proppant during fracturing. At very high shear rate however, in particular above 170 s^{-1}, the viscosity falls drastically allowing the fluid to be pumped down the wellbore. Also, the surfactant worm- or rod-like micelles tend to disaggregate by contact with hydrocarbons and, if no surfactant emulsion is effectively formed, the surfactant molecules are normally carried along the fracture, to the well bore, during the hydrocarbon backflow.

On the other hand, the leak-off rate of viscoelastic polymer-free fracturing fluids is high so that they are mainly used in connection with hydrocarbon bearing formations wherein the permeability of the formation rocks is low. In addition, the costs incurred by the use of high viscoelastic surfactant concentrations in aqueous wellbore service fluids and, in particular, in fracturing fluids, are elevated.

In the patent published the 21st of February 1984 under the number US-4,432,881, it is proposed to add thickening agents to, for example, fracturing fluids. In the patent published the 17th of September 1985 under the number US-4,541,935, the added thickening agent comprises a non-ionic surfactant and a hydrophobically-modified polymer.

SUMMARY OF THE INVENTION

Considering the above prior art, one problem that the invention is proposing to solve is to carry out an aqueous viscoelastic fluid for use in the recovery of hydrocarbons and, in particular, for use as a fracturing fluid, said fluid being responsive to hydrocarbons and comprising a limited quantity of surfactant and/or polymer, thereby reducing the costs involved in the use of said fluid.

As a solution to the above problem, the invention concerns, in a first aspect, an aqueous viscoelastic fluid for use in the recovery of hydrocarbons, comprising:

a viscoelastic surfactant; and

a hydrophobically-modified polymer,

wherein the viscoelastic surfactant concentration in said fluid is below its overlap concentration.

In a second aspect, the invention concerns an aqueous viscoelastic fluid for use in the recovery of hydrocarbons, comprising:

a viscoelastic surfactant; and

a hydrophobically-modified polymer,

wherein the hydrophobically-modified polymer concentration in said fluid is below its overlap concentration.

In a third aspect, the invention concerns a method for recovering hydrocarbons comprising the following step:

providing an aqueous viscoelastic fluid comprising a viscoelastic surfactant and a hydrophobically-modified polymer, wherein the viscoelastic surfactant concentration in said fluid is below its overlap concentration.

In a fourth aspect, the invention concerns a method for recovering hydrocarbons comprising the following step:

providing an aqueous viscoelastic fluid comprising a viscoelastic surfactant and a hydrophobically-modified polymer, wherein the hydrophobically-modified polymer concentration in said fluid is below its overlap concentration.

The hydrophobically-modified polymer and, notably, pendant hydrophobic chains of said polymer, interact with the surfactant micelles. As a result, a viscoelastic gel structure is created even at a viscoelastic surfactant and/or at a hydrophobically-modified polymer concentration below their/its overlap concentration, thereby reducing the costs associated with the use of the fluid, said fluid however remaining responsive to hydrocarbons.

In a further aspect, the invention concerns an aqueous viscoelastic fluid for use as a fracturing fluid, comprising: a viscoelastic surfactant; and a hydrophobically-modified polymer. Advantageously, the viscoelastic surfactant is a cleavable viscoelastic surfactant and the hydrophobically-modified polymer comprises cleavable pendant hydrophobic cleavable chains.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood in the light of the following description of non-limiting and illustrative embodiments, given with reference to the accompanying drawings, in which:

- the figure 1 illustrates the physical interactions existing between hydrophobically-modified polymers and rod-like surfactant micelles in a fluid according to the invention;
- the figure 2 compares the viscosity of different fluids as a function of the hydrophobically-modified guar concentration, for various viscoelastic surfactant concentrations at a shear rate of 100 s^{-1};
- the figure 3 compares the viscosity of different fluids as a function of the hydrophobically-modified guar concentration, for various viscoelastic surfactant concentrations at a shear rate of 0.1 s^{-1}
- the figure 4 compares the viscosity of different fluids as a function of the viscoelastic surfactant

concentration, for various hydrophobically-modified polymer concentrations, at a shear rate of 100 s^{-1};

- the figure 5 compares the rheograms of two different fluids, one comprising a viscoelastic surfactant without hydrophobically-modified polymer and the other comprising both, a viscoelastic surfactant and a hydrophobically-modified polymer;
- the figure 6 compares the viscosity of three different fluids comprising a hydrophobically-modified guar having different hydrophobic substitution degrees, as a function of the concentration of a cationic viscoelastic surfactant;
- the figure 7 shows three bottles that illustrate the reduced tendency to form emulsions for a fluid according to the invention compared to equivalent fluids without hydrophobically-modified polymer component or without the viscoelastic surfactant component;
- the figure 8 shows two bottles that illustrate the need of pendant hydrophobic chains on polymer backbone to create a synergy between the polymer network and the surfactant network and avoid a phase separation;
- the figure 9 and 10 compare the viscosity of a fluid comprising a hydrophobically-modified polymer and a cationic viscoelastic surfactant with a corresponding fluid comprising an anionic viscoelastic surfactant, as a function of the surfactant concentration.
- the figure 11 shows a route for synthesis of a hydrophobically-modified poly(ethylene-alt-maleic anhydride);
- the figure 12 compares the viscosity of four fluids comprising a hydrophobically-modified polymer and a viscoelastic surfactant as a function of the temperature; and
- the figure 13 shows a route for synthesis of a hydrophobically-modified chitosan.

DETAILED DESCRIPTION

The present invention concerns an aqueous fluid for use in the recovery of hydrocarbons such as oil and gas. This aqueous fluid is a wellbore service fluid such as a drilling fluid, a completion fluid, a work over fluid, a packer fluid or a conformance or permeability control fluid and, more particularly, a fracturing fluid.

The fluid according to the invention comprises a viscoelastic surfactant and a hydrophobically-modified polymer.

The surfactant is said viscoelastic because, unlike numerous surfactants which constitute Newtonian solutions with a viscosity slightly higher than water even at high concentrations, it is capable of forming viscoelastic fluids at a lower concentration. This specific rheological behaviour is mainly due to the types of surfactant aggregates that are present in the fluids. In the fluids with low viscosity, the surfactant molecules aggregate in spherical micelles whereas, in viscoelastic fluids, long micelles, which can be described as worm-like, thread-like or rod-like micelles, are present and entangle.

Even the viscoelastic surfactant concentration in said fluid is below the overlap concentration c* of said surfactant in an aqueous solution, the fluid of the invention is viscoleastic. In other words, the surfactant concentration in the fluid is below its concentration c* according to which the surfactant micelles present in a surfactant solution start to entangle and the viscosity of said solution start to increase. In the present invention, this overlap concentration is experimentally determined by the break point of a curve obtained from the plot of the viscosity of the surfactant solution as a function of the surfactant concentration determined under any shear rate and, for example, under a low shear rate of 0.1 s^{-1} or under a high shear rate of 100 s^{-1}.

The viscoelastic surfactant of the invention is usually ionic. It may be cationic, anionic or zwitterionic depending on the charge of its head group. When the surfactant is cationic, it is associated with a negative counterion which is, generally, Cl^-. When it is anionic, it is associated with a positive counterion, generally Na^+ or K^+ and, when it is zwitterionic, it is associated with both negative and positive counterions, generally Cl^- and Na^+ or K^+.

The viscoelastic surfactant may be, for example, of the following formulae:

$$R\text{-}Z$$

where R is the hydrophobic tail of the surfactant, which is a fully or partially saturated, linear or branched hydrocarbon chain of at least 18 carbon atoms and Z is the head group of the surfactant which can be $-NR_1R_2R_3^+$, $-SO_3^-$, $-COO^-$ or, in the case where the surfactant is zwitterionic, $-N^+(R_1R_2R_3\text{-}COO^-)$ where R_1, R_2 and R_3 are each independently hydrogen or a fully or partially saturated, linear or branched, aliphatic chain of at least one carbon atom, possibly comprising a hydroxyl terminal group.

It may be, in another example, a cleavable viscoelastic surfactant of the following formulae, which is disclosed in the application filed on the 13th of February 2001 under the number GB 0103449.5 not published at the filing date of the present patent application:

$$R\text{-}X\text{-}Y\text{-}Z$$

where R is the hydrophobic tail of the surfactant, which is a fully or partially saturated, linear or branched hydrocarbon chain of at least 18 carbon atoms, X is the cleavable or degradable group of the surfactant which is an acetal, amide, ether or ester bond, Y is a spacer group which is constituted by a short saturated or partially saturated hydrocarbon chain of n carbon atoms where n is at least equal to 1, preferably 2 and, when n is ≥ 3, it may be a straight or branched alkyl chain, and Z is the head group of the surfactant which can be $-NR_1R_2R_3^+$, $-SO_3^-$, $-COO^-$ or, in the case where the surfactant is zwitterionic, $-N^+(R_1R_2R_3-COO^-)$ where R_1, R_2 and R_3 are each independently hydrogen or a fully or partially saturated, linear or branched, aliphatic chain of at least one carbon atom, possibly comprising a hydroxyl terminal group. Due to the presence of the cleavable or degradable group, cleavable surfactants are able to degrade under downhole conditions.

A cationic viscoelastic surfactant suitable for the implementation of the invention is the N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride. In an aqueous solution comprising 4 wt% NaCl or 3 wt% KCl, this viscoelastic surfactant forms a gel containing worm-like micelles that entangle at concentrations between 1.5 and 4.5 wt%. These worm-like micelles degrade in spherical micelles when the gel is broken by hydrocarbon.

Anionic viscoelastic surfactants suitable for the implementation of the invention are monocarboxylates $RCOO^-$ such as oleate where R is $C_{17}H_{33}$ or di- or oligomeric carboxylates such as disclosed in the patent application filed on the 11 July 2001 under the number PCT/GB01/03131 not published at the filing date of the present patent application. These mono-, di- or oligomeric carboxylates form viscoelastic gels when in alkaline solution in the presence of added salts such as potassium chloride (KCl) or sodium chloride (NaCl). Worm-like micelles of said gel degrade to spherical micelles when the gel is broken by hydrocarbon.

The hydrophobic-modified polymer is soluble in water. It has an average molecular weight comprised between 10,000 and 10,000,000 g/mol and, preferably, between approximately 100,000 and approximately 1,000,000 g/mol. Above 1,000,000 and, definitely, above 10,000,000 g/mol, the polymer may form structures which are difficult to remove from the fracture during the subsequent backflow of formation fluids. Under 100,000 and, definitely, under 10,000 g/mol, the polymer concentration that would be necessary to obtain a fluid of the invention is likely to be too high hence increasing considerably the fluid associated costs.

Even if the hydrophobically-modified polymer concentration in said fluid is below the overlap concentration c* of said hydrophobically-modified polymer in an aqueous solution, the fluid of the invention is viscoelastic. In other words, the polymer concentration in the fluid is below the concentration according to which the polymer molecules present in a polymer solution start to form a gel network and the viscosity of said solution starts to increase. As for the surfactant, in the present invention, this overlap concentration is experimentally determined by the break point of a curve obtained from the plot of the viscosity of the polymer solution as a function of the polymer concentration under any shear rate and, for example, under a low shear rate of 0.1 s^{-1} or under a high shear rate of 100 s^{-1}.

The hydrophobically-modified polymer has a principal backbone and, randomly or not grafted on said principal backbone, at a substitution degree range comprised between 0.01 and 10 and, preferentially, between approximately 0.03 and approximately 5 weight percent, pendant hydrophobic chains. The polymer can be charged or non-charged, the charges being positive or negative and being located on the polymer backbone or on the pendant hydrophobic chains. If the hydrophobic substitution degree of the hydrophobically-modified polymer is too high, its solubility in water decreases. If it is too low, it becomes difficult to obtain a stable fluid with a sufficient viscosity. In fact, the substitution degree of the hydrophobically-modified polymer is adjusted with a view to obtain a satisfactory fluid viscosity with a sufficient polymer water solubility.

The principal polymer backbone can be of a biological nature. It can be, notably, a polysaccharide. Suitable polysaccharides for the implementation of the invention are starch or starch derivatives such as starch phosphate, starch succinate, aminoalkyl starch or hydroxypropyl starch; cellulose or cellulose derivatives as carboxymethyl cellulose, methyl cellulose, ethyl cellulose or hydroxypropylmethyl cellulose; chitin or chitin derivatives such as the chitosan or chitosan derivatives such as the N-carboxybutyl chitosan or the N-carboxymethyl chitosan; galactomannans, in particular, guar and guar derivatives as the carboxymethyl guar or the carboxymethyl hydroxypropyl guar derivatives. It can also be a synthetic polymer such as a polyanhydride, for example the poly(isobutylene-alt-maleic anhydride), the poly(ethylene-alt-maleic anhydride), the poly(ethylene-graft-maleic anhydride), a polyacrylamide, a polyacrylate, a polyacrylate/polyacrylamide copolymer, a polyether, a polyester, a polyamide or a polyvinylalcohol.

The pendant hydrophobic chains are preferentially fully or partially saturated linear or branched hydrocarbon chains comprising preferably approximately 12 to 24 carbon atoms and including advantageously a cleavable or degradable group such as an acetal, an amide, an ether or an ester bond.

An example of a non-charged hydrophobically-modified polymer, which appears convenient for the implementation of the invention, is a guar hydrophobically modified by non charged alkyl chains.

An example of a positively charged hydrophobically-modified polymer, where the charges are located on the polymer backbone, which also appears convenient for the implementation of the invention, is a hydrophobically-modified chitosan. This polymer can be synthesized with various hydrophobic substitution degrees following the route described by Yalpani, M. and Hall, *L.D. Macromolecules*, 1984, vol. 17, p. 272 which produces N-alkylated chitosan by reductive amination of the free amino groups of the chitosan or, following the route presented in the figure 13 and described in D. Plusquellec and al., ENSCR, Departement de Chimie Organique, An Efficient Acylation of Free Glycosylamines for the Synthesis of N-Glycosyl Amino Acids and N-Glycosidic Surfactants for Membranes Studies, *J. Carbohydrate Chemistry*, 1994, 13(5), 737-751, which, in such case, produces N-acylated chitosan with cleavable hydrophobic chains.

Further examples of hydrophobically-modified polymers suitable for the implementation of the invention are hydrophobically-modified polyanhydrides, which can be obtained by an amidation or an esterification reaction of a polyanhydride such as a poly(isobutylele-alt-maleic anhydride), a poly(ethylene-alt-maleic anhydride) or a poly(ethylene-graft-maleic anhydride), with, respectively, an amine or an alcohol chain comprising between approximately 12 and approximately 24 carbon atoms. These hydrophobically-modified polyanhydrides comprise carboxylic groups attached to their backbone, each carboxylic group being associated with one pendant hydrophobic chain. As a result, the hydrophobically-modified polyanhydrides are not only hydrophobic but also hydrophilic. Preferentially, the chemical structure of the pendant hydrophobic chains corresponds to and, more preferentially, matches, the hydrophobic tail of the surfactant molecules of the fluid. In such case, the whole chemical structure of the pendant hydrophobic chain and its associated carboxyl group forms an amphiphilic structure corresponding to or matching the surfactant molecule structure, said carboxylic group being analogous to the charged hydrophilic head of the surfactant molecule.

The figure 11 shows a poly(ethylene-alt-maleic anhydride) hydrophobically modified by oleyl pendant chains and a route for the synthesis of this hydrophobically-modified polymer. As shown on said figure, the hydrophobically-modified poly(ethylene-alt-maleic anhydride) comprises a carboxylic group $-COO^-$ attached to the carbon atom immediately adjacent to the carbon atom where is grafted the hydrophobic oleyl pendant chain. Thus, both the hydrophilic and hydrophobic structures of the viscoelastic surfactant is matched in the local structure of the hydrophilic and the hydrophobic groups on the polymer. In addition, the oleyl pendant chain comprises an amide bond, which is cleavable or degradable.

In addition to the surfactant and the hydrophobically-modified polymer, the fluid of the invention may comprise salts including, for example, inorganic salts such as the chlorides of ammonium, sodium and potassium present in concentrations of 1-10 wt% but typically 3 or 4 wt% or organic salts such as sodium salicylate. The fluid may also contain an organic solvent such as, for example, isopropanol, which may be used to liquefy the viscoelastic surfactant component.

The fluid of the invention is viscoelastic. For example, the viscoelasticity of the fluid may be measured by carrying out dynamic oscillatory rheological measurements on the composition as generally described in Barnes H.A. *et al., An Introduction to Rheology*, Elsevier, Amsterdam (1997). In a typical dynamic oscillatory experiment, the composition is sheared sinusoidally according to the following equation (1):

$$\gamma(t) = \gamma_{(max)} \sin \omega t \ldots\ldots (1)$$

Where $\gamma(t)$ is the strain, $\gamma(max)$ is the maximum strain, t is time and ω is the angular frequency. The shear stress, σ, is given by:

$$\sigma(t) = \sigma_{(max)} \sin(\omega t + \delta) \ldots\ldots (2)$$

where δ is the phase angle.

The relative inputs given by the elastic component (G′) and viscous component (G″) are resolved as follows. Expanding the sine function in equation (2) gives equations (3) and (4) as follows:

$$\sigma(t) = \sigma_{(max)} [\sin \omega t \cos\delta + \cos \omega t \sin\delta] \ldots\ldots (3)$$

$$\sigma(t) \equiv \gamma_{(max)} [G' \sin \omega t + G'' \cos \omega t] \ldots\ldots (4)$$

where $G' \equiv (\sigma_{(max)} / \gamma_{(max)}) \cos \delta$ and $G'' \equiv (\sigma_{(max)} / \gamma_{(max)}) \sin \delta$.

Equation (4) therefore defines two dynamic moduli: G′, the storage modulus or elastic component and G″, the loss modulus or viscous component of a composition having viscoelastic properties.

The fluid of the present invention is an aqueous viscoelastic gel, where the term "viscoelastic gel" as used herein means a composition in which the elastic component (G′) is at least as important as the viscous component (G″). In the evolution from a predominantly viscous liquid to a viscoelastic gel, the gel point can be defined by the time when the contribution from the elastic and viscous components becomes equal, i.e. G′ = G″; at and beyond this point in time, G′≥G″ and the phase angle, δ is ≥45°.

The viscoelasticity of the fluid of the invention is due to interactions between the hydrophobically-modified polymer and the surfactant micelles. These interactions, which are schematically illustrated in the figure 1, are physical hydrophobic-hydrophobic interactions.

Some interactions between polymers and surfactant molecules have been studied and corresponding results can be found in M. A. Winnik and A. Yekta, Associative polymers in aqueous solution, *Current Opinion in Colloid & Interface Science*, 1997, 2:424-436; U. Kästner and R. Zana, Interactions between quaternary ammonium surfactant oligomers and water-soluble modified guars, *Journal of Colloid and Interface Science*, 1999, 218:468-479; S. Biggs, J. Selb and F. Candau, Effect of surfactant on the solution properties of hydrophobically modified polyacrylamide, *Langmuir*, 1992, 838-847; A. Hill, F. Candau and J. Selb, Aqueous solution properties of hydrophobically associating copolymers, *Progress in Colloid & Polymer Science*, 1991, 84:61-65; O. Anthony, C. M. Marques and P. Richetti, Bulk and surface behavior of cationic guars in solutions of oppositely charged surfactants, *Langmuir*, 1998, 14:6086-6095; I. Iliopoulos, Association between hydrophobic polyelectrolytes and surfactants, *Current Opinion in Colloid & Interface Science*, 1998, 3:493-498; S. Panmai, R. K. Prud'homme and D. Peiffer, Rheology of hydrophobically modified polymers with spherical and rod-like surfactant micelles, Department of Chemical Engineering, Princeton University, Princeton, NJ, Exxon Research and Engineering Company, Annondale, NJ, 1997; and the patents published under the numbers US-4,975,482, US-5,036,136 and US-6,194,356. The teachings of these studies may, in some cases, be useful for the understanding of the interactions existing in the fluid of the invention.

The fluid of the invention is hydrocarbon-responsive so that the gel structure breaks down on contact or mixing with hydrocarbons. In such case, the viscosity of the gel decreases to value of about 100 cP or below, at a low shear rate.

The fluid of the invention has a leak-off rate which is below the leak-off rate of pure viscoelastic surfactant fluids of equivalent rheology. This is a very significant advantage which means that the responsive fluid of the invention can be used to fracture higher permeability formations as compared to the pure viscoelastic surfactant fluids. It is likely that, after gel degradation by interaction with hydrocarbons, the polymer may partially block pores in the invaded formations rocks which may hinder fracture clean-up relative to the pure viscoelastic surfactant fluid. However, it is also noted here that the clean-up performance of the fluid of the invention is likely to be similar or better than that observed for a linear polymeric fracturing fluid, i.e. the clean-up should be acceptable and superior to covalently crosslinked polymer fluids.

Practically, all compounds of the fluid of the invention are blended at surface together with the proppant, which can be, for example, a 20-40 mesh sand, bauxite or glass beads. When subjected to a very high shear rate, the viscosity of this fluid is sufficiently low to allow its pumping downhole. There, the pumped fluid, carrying the proppant, is injected into the formation rocks to be fractured under a high pressure. At that time, the fluid of the invention is sufficiently viscous for carrying the proppant through the fracture. The fluid then degrades by contact with hydrocarbons flowing through the fracture.

Example 1

Determination of the overlap concentrations of a surfactant and a hydrophobically-modified polymer and of the critical aggregation concentration of a blend comprising said surfactant and said hydrophobically-modified polymer - viscosity of a fluid comprising a surfactant and a hydrophobically-modified polymer

On figure 2 is plotted the viscosity of an aqueous solution of a hydrophobically-modified guar, 0, 1, 2 or 3 wt% of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride and 3 wt% of potassium chloride as a function of the concentration, calculated in wt %, of said hydrophobically-modified polymer, at 80 °C and under a high shear rate of 100 s^{-1}. The hydrophobic-modified guar has a molecular weight of 0.5 x 10^6 g/mol and comprises between 0.03 and 1.7 wt% of pendant linear hydrocarbon chains of 20 carbon atoms.

On figure 3 is plotted the viscosity of an aqueous solution of a hydrophobically-modified guar, 0, 1 or 2 wt% of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride and 3 wt% of potassium chloride as a function of the concentration, calculated in wt %, of said hydrophobically-modified polymer, at 80 °C and under a low shear rate of 0.1 s^{-1}. The hydrophobic-modified guar has a molecular weight of 0.5 x 10^6 g/mol and comprises between 0.03 and 1.7 wt% of pendant linear hydrocarbon chains of 20 carbon atoms.

On figure 4 is plotted the viscosity of an aqueous solution of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride, 0, 0.2, 0.5, 0.6, 0.7 or 1 wt% of the above hydrophobically-modified guar and 3 wt% of potassium chloride as a function of the concentration, calculated in wt %, of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride, at 80 °C and under a high shear rate of 100 s^{-1}.

From the particular curves of figures 2 and 3, wherein the concentration of the N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride is null, it can be deduced that the overlap concentration c* of the hydrophobically-modified guar is equal to about 0.63 wt% and, from the particular curve of the figure 4, wherein the concentration of the hydrophobically-modified polymer concentration is null, it can be deduced that the overlap concentration c* of the N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride is equal to about 1.5 wt%.

The overlap concentration of a blend of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride and the hydrophobically-modified polymer, that is to say the critical aggregation concentration (cac) of said blend, can be experimentally determined from the curves of the figures 2, 3 and 4, wherein increasing concentrations of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride or, respectively, increasing concentrations of the hydrophobic-modified polymer have been added, by determining the break point of the curve obtained from the plot of the viscosity as a function of the blend concentration at the high shear rate of 100 s^{-1} or low shear rate of 01. s^{-1}. For example, it appears that the cac of the blend of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride and the hydrophobically-modified polymer in an aqueous solution comprising 3 wt% KCl at 80°C and under a high shear rate of 100 s^{-1}, is obtained by using only 0.2 wt% of the hydrophobically-modified polymer and 1 wt% of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride.

Thus, a viscoelastic fluid according to the invention, comprising N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride and a hydrophobically-modified guar can be obtained at a concentration of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride below its overlap concentration. The concentration of the hydrophobically-modified guar can also be below its overlap concentration. Both the N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride and the hydrophobically-modified concentrations in the blend are such as the cac in said blend has been reached. The overlap concentration of the viscoelastic surfactant and the hydrophobically-modified polymer do not change significantly with the shear rate. This is not the case of the cac of the blend which varies as a function of the shear rate. The cac of the blend is slightly higher at high shear rate due to the breaking of some of the hydrophobically-modified polymer/surfactant interactions at such a shear.

The fact that the viscoelastic and the hydrophobically-modified polymer components are present at a concentration below their respective overlap concentrations has two major impacts: (1) the fluids of the invention are extremely cost-effective in terms of viscosity per unit weight of solutes, and (2) the fluids of the invention are highly responsive and easily broken by their interactions with hydrocarbons.

Example 2

Comparison of the rheogram of a fluid comprising a surfactant and a hydrophobically-modified polymer with the rheogram of a fluid comprising a surfactant only

The figure 5 compares the rheogram of an aqueous fluid of 3 wt% of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride and 3 wt% of potassium chloride with the rheogram of an aqueous fluid of only 1.3 wt% of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride, 0.6 wt% of the hydrophobic-modified guar of the example 1 and 3 wt% of potassium chloride, at 80°C.

The shear thinning rheograms are quite similar. Therefore, in the absence of hydrophobic-modified polymer, about 3 wt% N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride are required to obtain a fluid viscosity of 150 cP at a high shear rate of 100 s^{-1} whereas, in the presence of said polymer, at a concentration below its overlap concentration, the concentration of N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride can be reduced to only 1.3 wt%. That is below the overlap concentration of the pure N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride that has been determined as equal to about 1.5 wt% according to the example 1. That is below the overlap concentration of the hydrophobically-modified guar as well, that has been determined as equal to 0.7 wt% according to said example 1.

Example 3

Influence of the degree of hydrophobic substitution and of the length of the hydrophobic chain of the polymer

In the figure 6 is represented the viscosity of aqueous solutions of hydrophobic-modified guars of various hydrophobic substitution degrees, as a function of the concentration of N-erucyl-N,N,bis(2-hydroxyethyl)-N-methyl ammonium chloride. each aqueous solution comprises 3 wt% of potassium chloride and the viscosity is measured at 70 °C under a high shear rate of 100 s^{-1}. The hydrophobic-modified guar of the fluid referenced (a) has a molecular weight of about 0.5 x 10^6 g/mol, a substitution degree comprised between 0.03 and 1.7 wt% corresponding to 2 to 62 linear pendant alkyl C_{20} chains per polymer chain. The hydrophobic-modified guar of the fluid referenced (b) has also a molecular weight of about 0.5 x 10^6 g/mol. However, its substitution degree is higher than the substitution degree of the hydrophobic-modified guar of the fluid (a) and it comprises, in addition of long hydrocarbon chains of 20 carbon atoms, short hydrocarbon chains of only 12 carbon atoms. The hydrophobic-modified guar of the fluid (c) has a molecular weight lower than the molecular weight of hydrophobic-modified polymer of the fluids (a) and (b) but it has a higher hydrophobic substitution degree than the hydrophobic-modified polymer of the fluid (a). The pendant alkyl chains of the hydrophobically-modified polymer of the fluid (c) are linear of 20 carbon atoms.

The viscosity of fluid (b) is generally inferior to the viscosity of fluid (a) indicating that the presence of short hydrophobic chains of 12 carbon atoms does not improve the interaction between the polymer and the surfactant micelles. Since the hydrophobic tail of the surfactant is of 22 carbon atoms, it appears that the presence of hydrophobic pendant chains matching said hydrophobic tail improves the polymer/surfactant micelles interactions. The viscosity of fluid (c) is generally superior to the viscosity of fluid (a) indicating that increasing the degree of hydrophobic substitution of the polymer enhances the interactions between said polymer and the surfactant micelles, particularly for surfactant concentrations below its overlap concentration. This result is particularly interesting for the present invention as it is more easy to remove a low molecular weight polymer from the fracture during the subsequent backflow of the formation fluid compare to a higher molecular weight polymer.

Example 4

Fluid responsiveness to hydrocarbons

The fluid responsiveness to hydrocarbons has been tested using a bottle test. This test has been performed for three different fluids in the presence of oil mineral spirits of a boiling point fraction comprised between 179 and 210 °C. A volume of each fluid was placed at the bottom of a bottle, a same volume of oil was placed on top of the gel and each bottle was closed and heated in an oven at 60 °C for one hour. Each bottle was then visually inspected to determine if the gel had broken to its base viscosity. If not broken, gelled samples were shaken for 20 seconds and the bottles replaced in the oven for a further hour. This procedure was repeated until the gels had broken and the total time taken to this procedure was noted. Once the gel broken, the bottles were heated for a further period of 3 to 6 hours period without further mixing to determine if any emulsification was observable. If no emulsion formed, the bottles were shaken to promote such emulsification.

The first fluid was an aqueous fluid made of 0.7 wt% of the hydrophobically-modified guar of the fluid referenced (a) of the example 3, 3 wt% of N-erucyl-N,N,bis(2-hydroxyethyl)-N-methyl ammonium chloride and 3 wt% KCl, the second fluid was an aqueous fluid made of 3 wt% of N-erucyl-N,N,bis(2-hydroxyethyl)-N-methyl ammonium chloride and 3 wt% KCl and the third fluid was an aqueous fluid made of 0.7 wt% of a hydrophobic-modified guar and 3 wt% KCl.

By contact with oil, all the gels were broken after 2 to 3 hours and, in each bottle, we can see two phases, a lower phase comprising the broken gel and a higher phase comprising the oil. However, in the bottle containing the first fluid, which is shown, in the figure 7, on the left, the oil phase appears clear and no emulsion was observable whereas, in the two other bottles, the oil phase appears cloudy and an emulsion was observable.

Thus, the surfactant and hydrophobically-modified polymer containing aqueous fluid is responsive to hydrocarbon and no emulsion is formed after breaking. As a consequence, the clean-up of a fluid according to the invention after fracturing *per se*, during hydrocarbon backflow through the fracture, should be excellent.

Example 5

Need for pendant hydrophobic chains

A first bottle, shown on the left side of the figure 8 was filled with a first blend of 0.7 wt% of the hydrophobically-modified guar, 1 wt% of the viscoelastic surfactant used in the example 1 and 3 wt% KCl. A second bottle, shown on the right side of the figure 8 was filled with a second blend of 0.7 wt% of the non hydrophobically-modified guar, 1 wt% of the viscoelastic surfactant used in the example 1 and 3 wt% KCl.

One phase only can be distinguished in the first bottle whereas, in the second, two phases are present. Therefore, in the first bottle there is no phase separation as the hydrophobic associations between the hydrophobically-modified polymer and the viscoelastic surfactant stabilize the blend whereas, in the second bottle, there is a phase separation as there is no synergy between the non-modified polymer and the viscoelastic surfactant.

Example 6

Comparison between anionic and cationic surfactant containing fluids

On figure 9 is plotted the viscosity of an aqueous fluid comprising 0.6 wt% of the hydrophobically-modified guar of the example 1 and either, the cationic surfactant N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride or the anionic surfactant dimmer acid potassium chloride $C_{36}H_{66}O_4K_2$ as a function of the surfactant concentration, at 80°C and under a high shear rate of 100 s^{-1}.

The viscosity of the fluid containing the anionic surfactant is not as effective as the one obtained with the fluid containing the cationic surfactant. It is believed that this is due to differences in surfactant aggregate structure rather than to the difference in charge. The cationic surfactant can form worm-like micelles at 80°C whereas the anionic dimmer can not. A blend containing the same hydrophobically-modified guar but with an anionic surfactant which forms worm-like micelles at 80°C was then evaluated. This data is shown in figure 10. It can be now observed that the hydrophobically-modified polymer/cationic surfactant and hydrophobically-modified polymer/anionic surfactant blends have similar performances. This result confirms that it is the surfactant aggregate structure rather than the charge of the surfactant which influence its interaction with the hydrophobically-modified polymer.

In addition, tests identical to those of the example 4 were performed using the above fluids. It was shown that these fluids are responsive to hydrocarbons and that there was no emulsion.

Example 7

Fluid viscosity variations as a function of different parameters as the temperature

Hydrophobically-modified polyanhydrides of a molecular weight comprised between 100,000 and 500,000 g/mol were synthesized from the base polymer poly(ethylene-alt-maleic anhydride), according to the route presented in the figure 11. 1 to 5 wt% of the anhydride units of said hydrophobically-modified polyanhydrides were converted to oleyl amide carboxylate. These hydrophobically-modified polyanhydrides were blended with oleyl amide succinate, a cleavable surfactant having the same structure as the pendant hydrophobic/hydrophilic chain of the hydrophobically-modified polyanhydride. The oleyl amide succinate surfactant forms rod-like micelles at a concentration of 3 wt%, with 4 to 12 wt% KCl or NaCl.

The overlap concentration c*, considered under a shear rate of 0 s^{-1}, of the pure hydrophobically-modified polyanhydride has been shown to decrease from a value greater than 6, estimated to about 10, to about 2 wt% as the degree of hydrophobic substitution of said hydrophobically-modified polyanhydride increases from 1 to 5 %. For the same increase of hydrophobic substitution degree, the critical aggregation of a blend containing the hydrophobically-modified polymer and the oleyl amide succinate has been shown to decrease from 3 wt% to about 1.8 wt%.

In addition, it has been shown that the overlap concentration c*, considered under a shear rate of 0 s^{-1}, of the pure hydrophobically-modified polyanhydride, decreases on the addition of salt NaCl or KCl. In fact, increasing ionic strength of the hydrophobically-modified polymer solution reduces the repulsive effect of the charged hydrophobically-modified polymer thereby increasing the hydrophobic interactions.

At 80°C and under a high shear rate of 100 s^{-1}, the following viscosities are obtained for the following aqueous fluids, where the viscoelastic surfactant (VES) is the oleyl amide succinate and the hydrophobically-modified polymer (hm-P) is the hydrophobically-modified polyanhydride of the figure 11, substituted at 2.5 wt%:

Aqueous fluid composition	Fluid viscosity at a shear rate of 100 s^{-1} (cP)
4 wt% VES + 8 wt% KCl	300
3 wt% hm-P + 8 wt% NaCl	11.9
3 wt% hm-P + 0.6 wt% VES + 8 wt% NaCl	805

It appears that the viscosity of a fluid comprising both, a the oleyl amide succinate and the hydrophobically-modified polyanhydride is very high, even if the surfactant concentration is quite low.

At 120 °C, the viscosity of said fluid comprising both the oleyl amide succinate and the hydrophobically-modified polyanhydride decreases to 68 cP. However, at 150 °C, the viscosity increases to 132 cP.

The figure 12 compares the rheograms of aqueous fluids comprising 3 wt% of the hydrophobically-modified polyanhydride of the figure 11 with a substitution degree equal to 2.5, 8 wt% NaCl and 0, 0.2, 0.3 or 0.6 wt% of oleyl amide succinate, under a high shear rate of 100 s^{-1}, for temperatures comprised between 60 and 150°C.

The viscosity of the fluids comprising 0.2, 0.3 or 0.6 wt% of oleyl amide succinate is well above the viscosity of the fluid exempt of oleyl amide succinate. The fluids comprising oleyl amide succinate are typical viscoelastic gels from the ambient temperature to about 80 °C. Then, in the temperature range comprised between about 90 and about 130 °C, they behave as a viscous fluid before behaving as a viscoelastic gel in the temperature range comprised between about 140 and about 150 °C.

The reason why there is a decrease of the viscosity of the fluid for temperature up to about 110-120 °C and, for higher temperature an increase of the viscosity is not known with certitude. Nevertheless, the fact that the viscosity, at 150 °C is quite high appears interesting for the implementation of fluids according to the invention for fracturing of high temperature formations. As a result, the fluid of the invention is preferentially used in a temperature range between approximately 130 and approximately 160 °C.

Example 8

A fluid comprising a blend of hydrophobically-modified chitosan in solution in acetic acid, wherein the polymer backbone is positively charged, with N-erucyl-N,N,bis(2-hydroxyethyl)-N-methyl ammonium chloride has been prepared. This fluid appears also viscoelastic for surfactant and hydrophobically-modified polymer concentrations below their overlap concentrations.

CLAIMS

1. Aqueous viscoelastic fluid for use in the recovery of hydrocarbons, comprising:

   a viscoelastic surfactant; and

   a hydrophobically-modified polymer,

   wherein the surfactant concentration in said fluid is below its overlap concentration.

2. The fluid of claim 1, wherein the hydrophobically-modified polymer concentration is below its overlap concentration.

3. Aqueous viscoelastic fluid for use in the recovery of hydrocarbons, comprising:

   a viscoelastic surfactant; and

   a hydrophobically-modified polymer,

   wherein the hydrophobically-modified polymer concentration in said fluid is below its overlap concentration.

4. The fluid of claim 3, wherein the viscoelastic surfactant concentration is below its overlap concentration.

5. The fluid of one of the above claims, further comprising a salt.

6. The fluid of one of the above claims, wherein the viscoelastic surfactant aggregates are worm-like, thread-like or rod-like micelles.

7. The fluid of one of the above claims, wherein the viscoelastic surfactant is ionic.

8. The fluid of one of the above claims, wherein the viscoelastic surfactant is of the following formulae:

$$R\text{-}Z$$

where R is the hydrophobic tail of the surfactant, which is a fully or partially saturated, linear or branched hydrocarbon chain of at least 18 carbon atoms and Z is the head group of the viscoelastic surfactant which can be $-NR_1R_2R_3^+$, $-SO_3^-$, $-COO^-$ or, in the case where the surfactant is zwitterionic, $-N^+(R_1R_2R_3\text{-}COO^-)$ where R_1, R_2 and R_3 are each independently hydrogen or a fully or partially saturated, linear or branched, aliphatic chain of at least one carbon atom, possibly comprising a hydroxyl terminal group.

9. The fluid of one of the claims 1 to 7, wherein the viscoelastic surfactant comprises a head group and a hydrophobic tail and is of the following formulae:

$$R\text{-}X\text{-}Y\text{-}Z$$

where R is the hydrophobic tail of said viscoelastic surfactant, which is a fully or partially saturated, linear or branched, hydrocarbon chain of at least 18 carbon atoms; X is a degradable acetal, amide, ether or ester bond; Y is a spacer group, formed by a short fully or partially saturated hydrocarbon chain of at least one and preferentially 2 carbon atoms; and Z is the head group of the surfactant which can be $-NR_1R_2R_3^+$, $-SO_3^-$, $-COO^-$ or $-N^+R_1R_2R_3\text{-}COO^-$ where R_1, R_2 and R_3 are each independently hydrogen or a linear or branched saturated aliphatic chain of at least one carbon atom.

10. The fluid of one of the claims 1 to 7, wherein the viscoelastic surfactant is the N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride.

11. The fluid of one of the claims 1 to 6, wherein the viscoelastic surfactant is a mono-, a di- or an oligomeric carboxylate.

12. The fluid of one of the above claims, wherein the hydrophobically-modified polymer has an average molecular weight comprised between 10,000 and 10,000,000 g/mol and, preferentially, between approximately 100,000 and approximately 1,000,000 g/mol.

13. The fluid of one of the above claims, wherein the hydrophobically-modified polymer has a principal backbone and, grafted on said backbone, pendant hydrophobic chains.

14. The fluid of claim 13, wherein the pendant hydrophobic chains are grafted on the principal backbone at a substitution degree range comprised between 0.01 and 10 and, preferentially, between approximately 0.05 and approximately 5 wt%.

15. The fluid of claim 13, wherein the principal polymer backbone is a polysaccharide, a polyanhydride, a polyacrylamide, a polyacrylate, a polyacrylate copolymer, a polyether, a polyester, a polyamide or a polyvinylalcohol.

16. The fluid of claim 13, wherein the pendant hydrophobic chains are fully or partially saturated linear or branched hydrocarbon chains.

17. The fluid of claims 13, wherein the pendant chains are cleavable.

18. The fluid of one of the above claims, wherein the hydrophobically-modified polymer is a hydrophobically-modified chitosan.

19. The fluid of one of the above claims, wherein the hydrophobically-modified polymer is a hydrophobically-modified polyanhydride.

20. The fluid of one of the above claims, wherein said fluid is capable of forming a gel able to be broken down on contact or mixing with hydrocarbons.

21. The fluid of claim 20, wherein the gel is able to be broken with no emulsion formation.

22. The fluid of one of the above claims, wherein said fluid leak-off rate which is below the leak-off rate of a pure viscoelastic surfactant fluid of equivalent rheology.

23. The of one of the above claims, for use as a fracturing fluid.

24. Method for recovering hydrocarbons comprising the following step:
providing an aqueous viscoelastic fluid comprising a viscoelastic surfactant and a hydrophobically-modified polymer, wherein the viscoelastic surfactant concentration is below its overlap concentration.

25. The method of claim 24, wherein the hydrophobically-modified polymer concentration is below its overlap concentration.

26. Method for recovering hydrocarbons comprising the following step:
providing an aqueous viscoelastic fluid comprising a viscoelastic surfactant and a hydrophobically-modified polymer, wherein the hydrophobically-modified polymer concentration in said fluid is below its overlap concentration.

27. The method of claim 26, wherein the viscoelastic surfactant concentration is below its overlap concentration.

28. Aqueous viscoelastic fluid for use as a fracturing fluid, comprising:
a viscoelastic surfactant; and
a hydrophobically-modified polymer.

29. The fluid of claim 28, wherein the viscoelastic surfactant is a cleavable viscoelastic surfactant and the hydrophobically-modified polymer comprises cleavable pendant hydrophobic cleavable chains.

Application No: GB 0130880.8 33. **Examiner:** Kathryn Orme
Claims searched: 1,2,5-25,28-29 **Date of search:** 25 April 2002

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.T): E1F (FGP, FMB, FMC, FPA, FPC)
Int Cl (Ed.7): E21B 43/22, 43/26, 33/138, C09K 7/02
Other: Online: WPI, EPODOC, PAJ

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	WO 87/01758	(DOW CHEMICAL) see especially pages 5, 8 and 10	1-2, 5, 12-13, 15-16, 20, 22-25, 28-29
X	US 2001/0020531 A1	(VARADARAJ ET AL) see especially page 2 paragraphs 19-22 and page 3 lines 1-3	1-2, 5, 7-9, 13-16, 20, 24-25 and 28
X	US 6194356 B2	(JONES ET AL) see especially col 1 lines 12-15, col 3 lines 13-22, col 4 lines 25-36 and col 5 lines 1-30	1-2, 5-10, 12, 14, 20-25, 28-29
X	US 5566760 A	(HARRIS) see especially col 6 lines 44-67, col 7 lines 8-17, col 8 lines 47-64, col 9 lines 19-60	1-2, 7-9, 12-17, 20-25, 28-29
X	US 4432881 A	(EVANI) see especially col 3 lines 18-23, 49-65, col 4 lines 1-19, col 5 lines 1-37, col 6 lines 55-68, col 7 lines 1-34.	1-2, 5-9, 11-13, 15-17, 19-20, 23-25, 28

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
&	Member of the same patent family		

The Patent Office

INVESTOR IN PEOPLE

Application No: GB 0130880.8 34.
Claims searched: 1,2,5-25,28-29

Examiner: Kathryn Orme
Date of search: 25 April 2002

Category	Identity of document and relevant passage		Relevant to claims
X	US 4266610 A	(MEISTER) see especially col 1 lines 35-68, col 3 lines 42-63, col 5 lines 1-15	1-2, 5, 7-8, 13, 15-17, 19-20, 24-25 and 28

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
&	Member of the same patent family		