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VISCOUS HEAVY BRINES

The present invention relates to viscous brine solutions and, more particularly, to so called heavy brines having a density greater than 1.62 g/cm^3 .

5 In recent years, the practical operating range of clear brines for use in the oil and gas industry has been significantly extended by utilizing soluble zinc salts, particularly zinc bromide, so that the advantages of clear brines can now be obtained with fluids having densities
10 as high as 2.30 g/cm^3 at ambient temperatures and pressures.

The high density clear brines are used extensively: as completion fluids, to minimize plugging of perforation tunnels, to protect formation permeability, and to mini-
15 mize mechanical problems; as workover fluids, for the same reasons; as packer fluids, to allow easy movement and retrieval of the packer; or underreaming, gravel-pack and sand consolidation applications; as kill fluid on ballast fluid; for wire-line work; and as drilling fluids.

20 Clear brines having a density of up to 1.70 g/cm^3 are generally formulated to contain sodium chloride, sodium bromide, potassium chloride, calcium chloride, calcium bromide or mixtures of these salts. Clear brines having a density up to 1.81 g/cm^3 can be formulated with
25 calcium chloride and calcium bromide. If the brine must have a low crystallization temperature, however, clear brines in this density range are generally formulated to contain a soluble zinc salt. Zinc bromide is preferred because brines containing it are less corrosive than
30 brines containing zinc chloride. Clear brines having a density greater than 1.81 g/cm^3 are formulated to contain zinc bromide.

Viscous clear fluids are sometimes desired. Generally, hydroxyethyl cellulose (HEC) and xanthan gum poly-
35 mers are compatible with the fluids which do not contain zinc salts. At higher densities, however, the hydration

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of the viscosifiers is significantly slower. HEC is generally considered as unsatisfactory for use in fluids containing zinc salts.

It is an object of the present invention to provide
5 viscous heavy brine solutions, particularly such solutions containing zinc bromide and HEC.

Another object of this invention is to provide a method of increasing the rate of hydration of HEC in heavy brines, particularly those brines having a density greater
10 than 1.62 g/cm³.

Still another object of this invention is to provide a method of increasing the viscosity of a heavy brine by adding thereto an "activated" HEC, as disclosed more fully hereinafter, and a sequestrant.

15 The above and other objects of the present invention will become apparent from the description given herein and the appended claims.

This invention provides a method of increasing the viscosity of a heavy brine solution containing one or more
20 soluble salts selected from calcium chloride, calcium bromide, and zinc bromide, which comprises adding to said solution hydroxyethyl cellulose and from 0.25 to 20 g/l of a sequestrant selected from polyphosphonic acids, amino-polycarboxylic acids, polyhydroxy carboxylic acids, water
25 soluble salts thereof and mixtures thereof.

This invention also provides a method of increasing the rate of hydration of hydroxyethyl cellulose in a heavy brine solution containing one or more soluble salts selected from calcium chloride, calcium bromide, and zinc bromide, which comprises adding to said brine from 0.25 to
30 20 g/l of a sequestrant as defined above.

This invention further provides a viscous heavy brine solution containing hydroxyethyl cellulose, one or more soluble salts selected from calcium chloride, calcium
35 bromide and zinc bromide, and from 0.25 to 20 g/l of a sequestrant as defined above.

The present invention is based on the discovery

that the addition of certain sequestrants to heavy brine solutions increases the rate of hydration of HEC in the heavy brine and increases the viscosity of the heavy brine containing HEC.

5 The heavy brines for use in the present invention contain one or more soluble salts selected from calcium chloride, calcium bromide and zinc bromide. Brines containing only calcium chloride can be formulated having a density from 1.02 to 1.40 g/cm³. Brines containing only
10 calcium bromide can be formulated having a density from 1.02 to 1.70 g/cm³. However, because calcium chloride is much less expensive than calcium bromide, brines in the density range from 1.35 to 1.81 g/cm³ are generally formulated to contain both calcium chloride and calcium bromide
15 depending on the lowest temperature at which the brine will be used. Brines heavier than 1.80 g/cm³ are generally formulated to contain calcium chloride, calcium bromide, - and zinc bromide, or only calcium bromide and zinc bromide, depending on the lowest temperature at which the brines
20 will be used. Brines in the density range from 1.70 to 1.80 g/cm³ may be formulated to contain calcium chloride, calcium bromide, and zinc bromide, if brines having a lower crystallization point are desired.

 The most difficult brines to viscosify contain zinc
25 bromide, and these brines are preferred for use in the present invention. As indicated, such brines will generally have a density from 1.70 to 2.30 g/cm³.

 Generally, brines of any density within the range disclosed are prepared by mixing together various standard,
30 commercially available brines, as follows: calcium chloride brines having a density from 1.32 to 1.39 g/cm³; calcium bromide brine having a density of 1.70 g/cm³; and a calcium bromide/zinc bromide brine having a density of 2.30 g/cm³ containing about 20% by weight of calcium bromide and about 57% by weight of zinc bromide. Solid
35 anhydrous calcium chloride and solid calcium bromide are also used in conjunction with these brines to prepare the heavy brines for use in this invention. Standard brine

mixing tables are available from the various manufacturers of these brines.

The HEC polymers which are useful as viscosifiers in the present invention are solid, particulate materials which are water soluble or water dispersible and which upon solution or dispersion in an aqueous medium increase the viscosity of the system. HEC polymers are generally high yield, water soluble, non-ionic materials produced by treating cellulose with sodium hydroxide followed by reaction with ethylene oxide. Each anhydroglucose unit in the cellulose molecule has three reactive hydroxy groups. The average number of moles of the ethylene oxide that becomes attached to each anhydroglucose unit in cellulose is called moles of substituent combined. In general, the greater the degree of substitution, the greater the water solubility. In general, it is preferable to use HEC polymers having as high a mole substitution level as possible.

Usually, upon the addition of dry, powdered hydrophilic materials, such as HEC, to water, the polymer particles undergo hydration preventing the interior of the particle from readily hydrating, solvating or otherwise dispersing in the aqueous medium. Accordingly, high shear long mixing times and/or elevated temperatures must be applied in order to obtain a homogeneous system.

We have found that HEC and other hydrophilic polymers can be activated such that the polymers will viscosify heavy brines at ambient temperatures. Activated HEC compositions, and methods for activating HEC, are disclosed in our prior British Patent Applications No. 8101828 (Publication No. 2070611 A) and No. 8109880 (Publication No. 2075041 A). Methods of activating other hydrophilic polymers are disclosed in our prior British Patent Application No. 8125937 (Publication No. 2086923 A).

Activated HEC compositions comprise: (1) HEC, a solvating agent comprising a water miscible, polar organic liquid which when uniformly mixed with HEC in a weight ratio of HEC to solvating agent of 1:2 produces a mixture

with substantially no free liquid solvating agent present after remaining quiescent for one week at ambient temperature in a sealed container, and a diluting agent comprising an organic liquid which is not a solvating agent; and

- 5 (2) HEC, a water soluble organic liquid, and an aqueous liquid, the organic liquid when uniformly mixed with the HEC in a weight ratio of HEC to organic liquid of 1:2 produces a mixture with free liquid present after remaining quiescent for one week at ambient temperature in a sealed
10 container, the aqueous liquid having a pH greater than 7.0.

Generally speaking, it has been found that virtually any organic compound which passes the solvation test described above, will function, to a usable degree, as a solvation agent. Non-limiting but preferred solvating
15 agents include: aliphatic glycols containing from 2 to 5 carbon atoms, such as ethylene glycol, 1,2-propanediol, 1,4-butanediol, and 1,3-pentanediol; alkylene triols containing from 2 to 6 carbon atoms such as glycerol, 1,2,3-butanetriol and 1,2,3-pentanetriol; amides containing from
20 1 to 4 carbon atoms such as formamide, acetamide, and dimethyl formamide; and mixtures of the various above compounds.

The diluting agent, in general, will be any liquid organic compound or material which is not a solvating
25 agent. In general, the diluting agents are liquids which do not appreciably swell the HEC polymers, i.e. they do not produce semi-solid or viscous mixtures which have no free liquid present after the one week solvation period described in the above test for determining solvating agents.

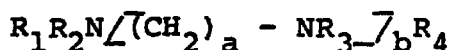
- 30 Non-limiting examples of diluting agents include liquid aliphatic and aromatic hydrocarbons containing from 5 to 10 carbon atoms, kerosene, diesel oil, isopropanol, alkylene glycol ethers, and vegetable oils. Particularly preferred are organic liquids which are water soluble or
35 miscible, most preferably alkanols having at least 3 carbon atoms, ethylene glycol monoalkyl ethers, and dialkylene glycol monoalkyl ethers. The diluting agent will

maintain the polymeric composition in a liquid, pourable state at a temperature of about 20°C. It will be understood, however, that lesser amounts of diluting agent can be used if desired, and that the ultimate amount of diluting agent employed will depend upon the type of shear which is available to disperse the thickener. In general it has been found that desirable thickeners, which are pourable liquids, can be produced from compositions containing from 10 to 25% by weight of HEC polymer, from 2 to 70% by weight of diluting agent, and from 5 to 88% by weight of solvating agent.

The concentration of HEC need only be a viscosity increasing amount. Generally, the heavy brines of this invention will contain 0.25 to 15 g/l, preferably 0.7 to 8.6 g/l of HEC.

The sequestrants which are employed according to the present invention are polyphosphonic acids, aminopolycarboxylic acids, polyhydroxy carboxylic acids, and their water soluble salts, particularly the alkali metal, ammonium, and alkanol ammonium salts thereof.

Representative, non-limiting, aminopolycarboxylic acids are compounds of the formula



where R_1 , R_2 , R_3 , and R_4 are independently H, $\text{---CH}_2\text{COOH}$, or $\text{---}(\text{CH}_2\text{CH}_2\text{O})_c\text{H}$, c is 1 to 5, a is 2 to 6, and b is 0 to 6, provided that at least one-half of the radicals represented by R_1 , R_2 , R_3 , and R_4 are $\text{---CH}_2\text{COOH}$.

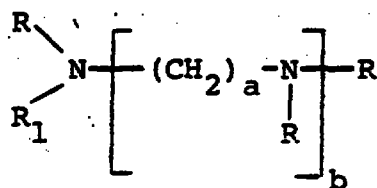
Representative, non-limiting, polyhydroxycarboxylic acids are citric acid and gluconic acid.

Representative, non-limiting, polyphosphonic acids are set forth in U.S. Patent No. 3,971,734.

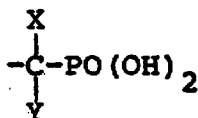
Preferred polyphosphonic acids are free acids and water soluble salts of the formula

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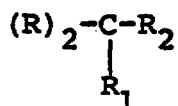
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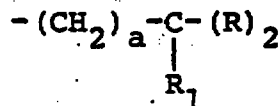
where each R is independently hydrogen, $-\text{CH}_2\text{PO}(\text{OH})_2$, or $-(\text{C}_n\text{H}_{2n}\text{O})_c\text{H}$ wherein n is 2 to 4 and c is 1 to 3; R_1 is



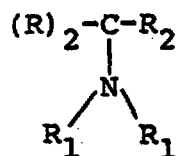
- 5 wherein X and Y are independently hydrogen or $\text{C}_1\text{-C}_4$ alkyl, a is 2 to 6 and b is 0 to 6; provided that at least 1/2 of the radicals represented by R are $-\text{CH}_2\text{PO}(\text{OH})_2$;



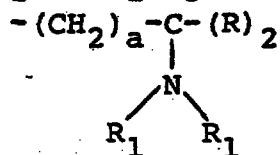
- 10 where R is $-\text{CH}_2\text{PO}(\text{OH})_2$, R_1 is hydrogen, hydroxyl, or $-(\text{C}_n\text{H}_{2n}\text{O})_c\text{H}$ wherein n is 2 to 4 and c is 1 to 3, and where R_2 is $\text{C}_1\text{-C}_5$ alkyl or a group of the formula



wherein a is 0 to 8; or

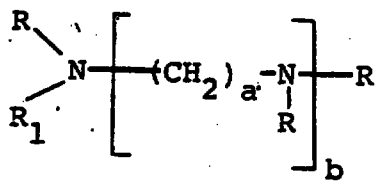


- 15 where R is $-\text{CH}_2\text{PO}(\text{OH})_2$, each R_1 is independently hydrogen, $-\text{CH}_2\text{PO}(\text{OH})_2$, or $(\text{C}_n\text{H}_{2n}\text{O})_c\text{H}$, wherein n is 2 to 4 and c is 1 to 3, and where R_2 is $\text{C}_1\text{-C}_5$ alkyl, and



wherein a is 0 to 8.

- 20 Most particularly preferred sequestering compounds are



where R is --CH₂PO(OH)₂, R₁ is --CH₂PO(OH)₂, a is either 2 or 6 and b is 0 to 4, especially those compounds wherein b is 0 or wherein a is 6 and b is 1 to 4.

5 Other water soluble polyphosphonates that contain at least two phosphonic acid groups per molecule which may be used in the practice of this invention are disclosed in U.S. Patents No. 3,733,270; 3,674,804; 3,576,783; 3,556,762; 3,551,339; 3,549,728; 3,497,313; 3,440,148; and 3,400,176.

10 The concentration of sequestrant useful in the practice of this invention will be an amount sufficient to increase the rate of hydration of HEC in the heavy brine which is desired to be viscosified. Concentra-
tions of sequestrant from 0.25 to 20 g/g are sufficient.

15 To illustrate the present invention more fully, the following non-limiting Example is presented. All physical property measurements were made in accordance with testing procedures set forth in STANDARD PROCEDURE FOR TESTING DRILLING FLUID, API RP 13B, Seventh Edition, April, 1978.

20 The physical property parameters referred to in the Example are in units expressed as follows:

- Apparent viscosity = centipoise
- Plastic viscosity = centipoise
- Yield Point = Kg/m²
- 25 10-Sec. Gel Strength = Kg/m²

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Example of the Invention

An activated HEC gellant was prepared by mixing together 124.5 parts by weight of isopropyl alcohol, 0.5 parts by weight of CAB-O-SIL M5 fumed silica, 50.0 parts by weight of NATROSOL 250 HHR hydroxyethyl cellulose, and 75.0 parts by weight of ethylene glycol. A 1.86 g/cm^3 $\text{CaBr}_2/\text{ZnBr}_2$ solution was prepared by mixing a 1.70 g/cm^3 CaBr_2 solution with a 2.30 g/cm^3 $\text{CaBr}_2/\text{ZnBr}_2$ solution in a 0.74/0.26 volume ratio. Other 1.86 g/cm^3 $\text{CaBr}_2/\text{ZnBr}_2$ solutions were prepared similarly, except that a 50% by weight aqueous solution of nitrilotri (methylenephosphonic acid) was added in varying amounts to the 2.30 g/cm^3 solution before its dilution with the 1.70 g/cm^3 solution. The concentration of nitrilotri (methylenephosphonic acid) in the 1.86 g/cm^3 brines was 2.40, 5.89, and 20.74 g/l as indicated in Table 1. Thereafter, the brines were viscified with 5.72 g/l of HEC (28.6 g/l of the activated gellant composition) by mixing with a Multimixer for 15 minutes. Fann viscosities were then obtained, after the solutions had hydrated for 90 hours at room temperature, and after the solutions were hot rolled for 16 hours at 65.5°C . The data obtained are given in Table 1.

The data indicate that the sequestrant increased the rate of hydration of the HEC and significantly increased the viscosity of the viscified brine. However, the brine containing 20.74 g/l of this sequestrant had poor thermal stability as evidenced by the decrease in viscosity on rolling at 65.5°C .

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TABLE I

5.72 g/l HEC

g/l Nitritoltri (methylenephosphonic acid)

<u>Fann V-G Rheology</u>		<u>0</u>	<u>2.40</u>	<u>5.89</u>	<u>20.74</u>
<u>After 15 Minutes Mixing</u>					
5	600 rpm	62	99	125	138
	300 rpm	39	67	86	95
	Apparent Viscosity (cp)	31	49	62	69
	Plastic Viscosity (cp)	23	32	39	43
	Yield Point (Kg/m ²)	0.78	1.71	2.29	2.54
10	10-Sec. Gel Strength (Kg/m ²)	0.05	0.15	0.20	0.24
<u>After 90 Hours Hydration</u>					
15	600 rpm	136	185	240	280
	300 rpm	88	121	168	203
	Apparent Viscosity (cp)	78	92	120	140
	Plastic Viscosity (cp)	48	64	72	77
	Yield Point (Kg/m ²)	1.95	2.78	4.69	6.15
	10-Sec. Gel Strength (Kg/m ²)	0.20	0.54	1.51	2.05
<u>After Rolling Overnight at 65.5°C</u>					
20	600 rpm	177	239	246	141
	300 rpm	124	164	184	82
	Apparent Viscosity (cp)	88	119	123	70
	Plastic Viscosity (cp)	53	75	62	59
	Yield Point (Kg/m ²)	3.47	4.34	5.96	1.12
25	10-Sec. Gel Strength (Kg/m ²)	0.68	1.17	1.71	0.07
<u>% Hydration in 15 Minutes*</u>		31.5	40.9	46.7	115.9

* % Hydration in 15 Minutes = $\frac{300 \text{ rpm Reading After 15 Minutes} \times 100}{300 \text{ rpm Reading After Rolling @ 65.5}^\circ\text{C}}$

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CLAIMS:

1. A method of increasing the viscosity of a heavy brine solution containing one or more soluble salts selected from calcium chloride, calcium bromide, and zinc bromide, which comprises adding to said solution hydroxyethyl cellulose and from 0.25 to 20 g/l of a sequestrant selected from polyphosphonic acids, aminopolycarboxylic acids, polyhydroxy carboxylic acids, water soluble salts thereof, and mixtures thereof.
2. A method as claimed in Claim 1 wherein the hydroxyethyl cellulose is added to the brine as an activated gellant composition in which the hydroxyethyl cellulose has been activated to hydrate in heavy brines at ambient temperatures.
3. A method as claimed in Claim 1 or 2 wherein the concentration of hydroxyethyl cellulose is from 0.25 to 15 g/l.
4. A method as claimed in any preceding Claim wherein the sequestrant is nitrilotri (methylenephosphonic acid) or a water soluble salt thereof.
5. A method of increasing the rate of hydration of hydroxyethyl cellulose in a heavy brine solution containing one or more soluble salts selected from calcium chloride, calcium bromide and zinc bromide, which comprises adding to said brine from 0.25 to 20 g/l of a sequestrant, selected from polyphosphonic acids, aminopolycarboxylic acids, polyhydroxy carboxylic acids, water soluble salts thereof, and mixtures thereof.
6. A method as claimed in Claim 5 wherein the brine contains from 0.25 to 15 g/l of hydroxyethyl cellulose.



7. A method as claimed in Claim 5 or 6 wherein the sequestrant is nitrilotri (methylenephosphonic acid) or a water soluble salt thereof.

8. A viscous heavy brine solution containing
5 hydroxyethyl cellulose, one or more soluble salts selected from calcium chloride, calcium bromide and zinc bromide, and from 0.25 to 20 g/l of a sequestrant selected from polyphosphonic acids, aminopolycarboxylic acids, polyhydroxy carboxylic acids, water soluble salts thereof,
10 and mixtures thereof.

9. A viscous heavy brine as claimed in Claim 8 which comprises from 0.25 to 15 g/l of hydroxyethyl cellulose.

10. A viscous heavy brine as claimed in Claim 8 or
15 9 wherein the sequestrant is nitrilotri (methylenephosphonic acid) or a water soluble salt thereof.

11. A method as claimed in Claim 1 or 5 and substantially as hereinbefore described with reference to the Example.

20 12. A viscous heavy brine as claimed in Claim 8 and substantially as hereinbefore described with reference to the Example.
