

HYDROXYETHYL CELLULOSE COMPOSITION FOR
VISCOSIFYING BRINES

The present invention relates to activated hydroxyethyl cellulose compositions for use as a viscosifier in brines, more particularly, so called heavy brines having a density greater than 1.618 g/ml.

Thickened aqueous liquids, particularly those containing oil field brines, are commonly used as well servicing fluids, such as drilling fluids, workover fluids, completion fluids, packer fluids, well treating fluids, subterranean formation-treating fluids, spacer fluids, hole abandonment fluids, and other aqueous fluids in which an increase in viscosity is desired. It is known to use hydrophilic polymeric materials, such as hydroxyethyl cellulose (HEC), as thickening agents for aqueous liquids used in such well servicing fluids. HEC is not however, readily hydrated, solvated or dispersed in aqueous systems having a density greater than 1.618 g/ml without the use of elevated temperatures and/or mixing under high shear for extended periods of time. For example, hydroxyethyl cellulose polymers are poorly hydrated, solvated or dispersed in such aqueous solutions containing one or more multivalent-cation water soluble salts, such as heavy brines which are commonly used in well servicing fluids. In many instances, for example in workover operations, the equipment available for preparing the well servicing fluids does not readily lend itself to high temperature, high shear mixing. Accordingly, it is usually necessary, if it is desired to use such thickened brines, to prepare them off the well site.

The prior art indicates that it is known to slurry HEC in an organic medium, such as ethylene glycol or an alcohol, before adding the HEC to an aqueous liquid in order to obtain good dispersion of the HEC. The prior art also indicates that HEC is swollen in certain organic

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liquids, including ethylene glycol. When HEC is slurried in ethylene glycol or an organic liquid which swells the HEC, the prior art indicates that the slurry must be added to the aqueous liquid immediately or the HEC will swell
5 resulting in poor dispersion in the aqueous liquid. Thus, the use of ethylene glycol and other organic liquids which swell the HEC, is not recommended for slurrying the HEC.

It is disclosed in our prior British Patent Application No. 8101828 (Publication No. 2070611 A) that HEC
10 can be dispersed and hydrated in heavy brines by slurrying it with a polar organic liquid which swells the HEC and an organic liquid which does not swell the HEC, and thereafter aging the mixture.

We have now found that HEC can be activated so that
15 it will hydrate readily in heavy brines at ambient temperatures, by slurrying the HEC in an organic liquid which swells the HEC and aging the slurry.

The present invention provides a viscosifying composition which comprises a polar organic liquid containing from 10 to 25% by weight, based on polar
20 organic liquid, of hydroxyethyl cellulose in a polar organic liquid, which polar organic liquid when uniformly mixed with hydroxyethyl cellulose in a weight ratio of hydroxyethyl cellulose to
25 polar organic liquid of 1:2, produces a mixture with substantially no free liquid present after remaining quiescent for one week at ambient temperature in a sealed container, said composition having been aged for a period of time sufficient to activate
30 the hydroxyethyl cellulose such that the hydroxyethyl cellulose will hydrate in heavy brines having a density greater than 1.618 g/ml. at ambient temperature.

The present invention also provides a process of activating hydroxyethyl cellulose such that
35 the hydroxyethyl cellulose will hydrate in heavy brine having a density greater than 1.618 g/ml at ambient temperature which comprises slurrying

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said hydroxyethyl cellulose at a concentration from 10 to 25% by weight in a polar organic liquid, and aging said slurry for a period of time sufficient to activate said hydroxyethyl cellulose, said

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polar organic liquid being one which, when uniformly mixed with hydroxyethyl cellulose in a weight ratio of hydroxyethyl cellulose to polar organic liquid of 1:2, produces a mixture with substantially no free liquid present after
5 remaining quiescent for one week at ambient temperature in a sealed container.

The present invention further provides a process of increasing the viscosity of an aqueous solution having a density greater than 1.618 g/ml which comprises mixing
10 said solution with a viscosifying composition as described above.

The concentration of HEC is from 10 to 25% by weight, preferably 10 to 20% by weight. Preferably also, the composition has been aged for at
15 least two hours at ambient temperatures.

Activation of HEC such that the HEC will hydrate in heavy brines at ambient temperatures is accomplished by the present invention as follows: the particulate HEC is first mixed with a polar organic liquid (POL) which swells the
20 HEC and thereafter the mixture is aged for a period, preferably at least two hours, at ambient temperature.

Many compounds can be utilized as the POL, depending upon the end use of the thickening agent. In determining whether a particular compound or material will
25 function as a POL according to the present invention, a simple test can be utilized as follows: one (1) part by weight of the HEC polymer is uniformly mixed, e.g. by spatulating, with two (2) parts by weight of the candidate POL. The mixture is then allowed to set, in a
30 quiescent state, for one week at ambient temperature in a container, preferably sealed. Liquids which are useful as the POL when subjected to this test procedure produce solid, semi-solid or viscous mixtures with substantially no free liquid present in the mixture after the one week
35 solvation period. Generally speaking, it has been found that virtually any organic compound which passes this solvation test described above, will function, to a usable

degree, as a POL. Non-limiting but preferred POLs include: aliphatic glycols containing from 2 to 5 carbon atoms such as ethylene glycol, 1,2-propanediol, 1,4-butanediol, or 1,3-pentanediol; alkylene triols containing
5 from 2 to 6 carbon atoms such as glycerol, 1,2,3-butane-triol, or 1,2,3-pentanetriol; amides containing from 1 to 4 carbon atoms such as formamide, acetamide, or dimethyl formamide; and mixtures of the various above compounds.

When formulating the viscosifying agents of the
10 present invention, it is preferable for ease of handling that the POL be present in an amount such that the viscosifying agent, i.e., the activated HEC composition, remains a pourable liquid after aging for a period of time sufficient to activate the HEC. Thus, ethylene glycol and
15 glycerol, which are the preferred polar organic liquids for use in this invention, produce pourable liquid viscosifiers at concentrations greater than 80% by weight. Other less efficient POLs may produce pourable liquid viscosifiers at concentrations greater than 75% by weight.
20 A concentration of POL greater than 90% by weight would generally be excessive and unnecessary. Thus, the concentration of HEC in the viscosifier composition should be in the range from 10 to 25% by weight, preferably from 10 to 20% by weight.

25 The mixture of HEC and POL is activated for use in viscosifying heavy brines by allowing the mixture to age, preferably for at least two hours at ambient temperature, more preferably for at least three hours. The activation may be accomplished in a shorter period of time at elevated temperatures. It has been found that if the concentration of HEC in the POL is such that a gelled composition is obtained upon activation, then the viscosifier composition decreases in gelling efficiency and may be completely ineffective upon further aging of the composition.
30
35 tion. Thus, the activated HEC compositions should be utilized before the composition gels.

The activated HEC composition can be utilized

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wherever HEC is required. However, activation of the HEC is necessary only when using the HEC in heavy brines having a density greater than 1.618 g/ml. 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 as high as 2.300 g/ml at ambient temperatures and pressures.

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

15 Clear brines having a density of 1.702 g/ml or lower 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 1.809 g/ml can be formulated with calcium chloride and calcium bromide; but if the brine must have a low crystallization temperature, then 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 brines containing zinc chloride. Clear brines having a density greater than 1.809 g/ml are formulated to contain zinc bromide.

20 The HEC will generally be present in the heavy brine at a concentration from 2.5 to 15 g/l.

25 To more fully illustrate the invention, the following non-limiting example is presented.

Example

Three samples respectively containing 10, 15 and 20% by weight of NATROSOL^(ATM) 250 HHR in ethylene glycol were prepared by mixing the HEC and ethylene glycol together for 30 seconds. Each sample was immediately evaluated at 2.86 g/l in a 1.917 g/ml $\text{CaBr}_2/\text{ZnBr}_2$ solution by hand shaking the sample and solution together for 30 seconds, and stirring the mixture on a Fann V-G meter at 300 rpm. The 300 rpm dial reading was taken after 30 and 60 minutes as indicated in Table 1, and after rolling the brines overnight at 65.5°C. Thereafter each sample was evaluated after aging for certain periods as indicated in Table 1.

The data indicate that the samples must be aged in order for the HEC to hydrate in this solution. The sample containing 10% by weight of HEC remained pourable for 48 hours. The sample containing 15% by weight of HEC was very viscous but could be used. The sample containing 20% by weight of HEC became excessively gelled after aging for a sufficient period to activate the HEC such that the gelled particles formed lumps and would not disperse, even after hot rolling.

A preferred minimum aging time at ambient temperature of 2 hours, more preferably at least 3 hours, is indicated, by these results. Shorter times will be effective at higher temperatures.

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Table 1

No. (2)		Aging Time Hours		Brookfield Viscosity cp. @ 6 rpm		Qualitative Sample Viscosity		2.86 g/l HEC in 1.917 g/ml Solution			
								300 rpm Fann V-G Dial Reading		A.R. (1)	
								Mixing Time, Minutes			
A								0	30	60	
		0		55		Pourable		8	9	9	68
		1		160		Pourable		9	13	15	70
		2		850		Pourable		9	15	19	73
		3		2,250		Pourable		11	18	22	75
		5		3,250		Pourable		10	18	23	74
		7		3,400		Pourable		10	20	25	76
		24		4,075		Pourable		11	19	24	76
		48		4,175		Pourable		11	20	26	76
		288		4,325		Pourable		12	24	31	67
B		0		100		Pourable		9	9	9	-
		1		1,675		Pourable		9	12	14	-
		2		25,000		Flowable		10	17	21.5	75
		3		51,500		Flowable		13	18	22	74
		5		70,000		Flowable		9	18	23	73
		7		77,500		Flowable		11	20	25	74
		24		86,500		Flowable		10	17	23	72
		48		OS		Flowable		10	20	25	75
		288		OS		Gelled		10	23	32	66
C		0		2,900		Pourable		9	9	9	-
		1		3,800		Pourable		8	9	10	72
		2		OS		Flowable		10	14	17	74
		3		OS		Gelled		9	17	21	73
		5		OS		Gelled		10	17	22	73
		7		OS		Gelled		9	11	12	62
		24		OS		Gelled		8	10	10	18
		48		OS		Gelled		8	8	8	11
		288		OS		Gelled		8	8	8	11

(1) Brine rolled overnight at 65.5°C.

(2) Sample A = 10% NATROSOL 250 HHR, 90% Ethylene Glycol
Sample B = 15% NATROSOL 250 HHR, 85% Ethylene Glycol
Sample C = 20% NATROSOL 250 HHR, 80% Ethylene Glycol
5 (all percentages by weight).

(3) OS = > 100,000



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CLAIMS:

1. A viscosifying composition which comprises a polar organic liquid containing from 10 to 25% by weight, based on polar organic liquid, of hydroxyethyl cellulose in a polar organic liquid, which polar organic liquid when uniformly mixed with hydroxyethyl cellulose in a weight ratio of hydroxyethyl cellulose to polar organic liquid of 1:2, produces a mixture with substantially no free liquid present after remaining quiescent for one week at ambient temperature in a sealed container, said composition having been aged for a period of time sufficient to activate the hydroxyethyl cellulose such that the hydroxyethyl cellulose will hydrate in heavy brines having a density greater than 1.618 g/ml. at ambient temperature.

15 2. A composition as claimed in Claim 1 wherein the concentration of hydroxyethyl cellulose is from 10 to 20% by weight.

20 3. A composition as claimed in Claim 1 or 2 wherein the polar organic liquid is an aliphatic glycol containing from 2 to 5 carbon atoms, an alkylene triol containing from 3 to 5 carbon atoms, an amide containing from 1 to 4 carbon atoms; or a mixture thereof.

25 4. A composition as claimed in Claim 3 wherein the polar organic liquid is ethylene glycol, glycerol, or a mixture thereof.

30 5. A composition as claimed in any preceding Claim, which has been aged for at least two hours at ambient temperature.

35 6. A composition as claimed in any preceding Claim which has been aged for at least three hours at ambient temperature.



7. A composition as claimed in Claim 5, wherein the concentration of hydroxyethyl cellulose is such that said composition is a pourable liquid after activation.

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8. A process of activating hydroxyethyl cellulose such that the hydroxyethyl cellulose will hydrate in heavy brine having a density greater than 1.618 g/ml. at ambient temperature which comprises slurring
10 said hydroxyethyl cellulose at a concentration from 10 to 25% by weight in a polar organic liquid, and aging said slurry for a period of time sufficient to activate said hydroxyethyl cellulose, said polar
15 organic liquid being one which, when uniformly mixed with hydroxyethyl cellulose in a weight ratio of hydroxyethyl cellulose to polar organic liquid of 1:2, produces a mixture with substantially no free
liquid present after remaining quiescent for one week at ambient temperature in a sealed container.

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9. A process as claimed in Claim 8 wherein the concentration of hydroxyethyl cellulose is from 10 to 20% by weight.

25 10. A process as claimed in Claim 8 or 9 wherein the polar organic liquid is an aliphatic glycol containing from 2 to 5 carbon atoms, an alkylene triol containing from 3 to 5 carbon atoms, an amide containing from 1 to 4 carbon atoms, or a mixture
30 thereof.

11. A process as claimed in Claim 10 wherein the polar organic liquid is ethylene glycol, glycerol, or a mixture thereof.

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12. A process as claimed in any of Claims 8 to 11 wherein the period of time is at least 2 hours at ambient temperature.



13. A process as claimed in Claim 12 wherein the period of time is at least 3 hours at ambient temperature.

5 14. A process as claimed in Claim 12 wherein the concentration of hydroxyethyl cellulose is such that said composition is a pourable liquid after activation.

10 15. A process of increasing the viscosity of an aqueous solution having a density greater than 1.618 g/ml. which comprises mixing said solution with a viscosifying composition as claimed in any of Claims 1 to 7.

15 16. A viscosifying composition as claimed in Claim 1 and substantially as hereinbefore described with reference to the Example.

20 17. A process as claimed in Claim 8 and substantially as hereinbefore described with reference to the Example.

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