

HYDRATED HYDROXYETHYL CELLULOSE COMPOSITIONS

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 2.3 g/cm^3 at ambient temperatures and pressures.

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.

Clear brines having a density of 1.7 g/cm^3 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 1.81 g/cm^3 can be formulated with calcium chloride and calcium bromide. If, however, 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 1.81 g/cm^3 are formulated to contain zinc bromide.

Viscous clear fluids are sometimes desired. It is known to use hydrophilic polymeric materials such as hydroxyethyl cellulose (HEC) as thickening agents for aqueous media used in such well servicing fluids. However, HEC is not readily hydrated, solvated or dispersed in aqueous systems having a density greater than 1.6 g/cm^3 without elevated temperatures and/or mixing under high shear for extended periods of time. For example,

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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. Moreover, HEC is generally considered as unsatisfactory and ineffective in heavy brines containing zinc bromide.

It is, therefore, an object of the present invention to provide new, polymeric compositions useful for thickening aqueous mediums, especially heavy brines having a density greater than 1.6 g/cm^3 .

A further object of the present invention is to provide an improved, aqueous well servicing fluid.

Still another object of the present invention is to provide a liquid polymeric composition which is pourable and pumpable, easily handled and which can be used to form viscous aqueous well servicing fluids under conditions of low shear mixing.

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

In accordance with the present invention, there is provided, in one embodiment, a viscosifying composition which will hydrate in and viscosify heavy brines having a density greater than 1.6 g/cm^3 at ambient temperatures which comprises an oleaginous liquid, and aqueous phase comprising water and an inorganic salt which has an exothermic heat of solution the concentration of inorganic salt being greater than 10% by weight of the aqueous phase,

a compatibilizing agent, and hydroxyethyl cellulose.

In another embodiment of the present invention, there is provided a method of activating hydroxyethyl cellulose such that said hydroxyethyl cellulose will hydrate in heavy brines having a density greater than 1.6 g/cm³ at ambient temperatures which comprises mixing an oleaginous liquid and a compatibilizing agent together to form a viscous slurry, mixing the slurry with an aqueous phase comprising water and an inorganic salt which has an exothermic heat of solution the concentration of inorganic salt being greater than 10% by weight of the aqueous phase, and then with hydroxyethyl cellulose to form a viscous pourable composition.

Still another embodiment of the present invention is to provide viscous well servicing fluids comprising a heavy brine solution having a density greater than 1.6 g/cm³ and a viscosifying amount of the viscosifying composition defined above.

The novel, liquid polymer containing compositions of the present invention utilize hydroxyethyl cellulose (HEC) as the primary component to effect thickening of aqueous liquids. Hydroxyethyl cellulose is a high yield, water soluble nonionic polymer 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 ethylene oxide that become 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. While HEC having a mole substitution level as low as 1.5 can be used, it is preferable to use HEC having a mole substitution level of 1.8 or greater, especially 2.5 and greater. It will be understood, that the particular HEC chosen will depend upon the type of liquid polymer composition, and ultimately the type of well drilling or treating fluid, desired. For example, so called surface

treated HEC such as described in U.S. Patents Nos. 3,455,714; 2,879,268; and 3,072,035 can be used with advantage. Such surface treated HEC exhibits greater dispersability in the composition.

5 The HEC is preferably present in the polymer containing composition in amounts from 10 to 30% by weight, based on the total composition, and more preferably, from 15 to 25% by weight, based on the total composition.

10 The oleaginous liquid used in preparing the compositions of the present invention can, in general, be any hydrophobic liquid which does not cause significant swelling or thickening of the HEC. Exemplary oleaginous liquids include liquid aliphatic and aromatic hydrocarbons particularly those having 5 to 10 carbon atoms, diesel oil, kerosene, petroleum distillates, and petroleum oils. Generally speaking, the oleaginous liquid will
15 be non-polar and have a low pour point. The oleaginous liquid is preferably present in the composition of the present invention in amounts from 35 to 55% by weight, based on the total weight of the composition, and more preferably from 40 to 50% by weight, based on the total weight of the composition.

20 The liquid, polymer-containing compositions of the present invention also contain a compatibilizing agent for effecting gelation or thickening of the hydrophobic liquid, emulsification of the aqueous phase, and compatibilizing of the HEC with the composition.

25 Non-limiting examples of compatibilizing agents include organophilic hectorites, organophilic attapulgites, and organophilic sepiolites. Such organophilic clays are produced by methods, and have a composition, described in U.S. Patents No. 2,966,506 and 4,105,578. In addition, the compatibilizing agent can include
30 finely divided siliceous materials such as fumed silica, and surface treated silicas such as silane-treated silicas. Particularly preferred compatibilizing agents are the organophilic clays described in U.S. Patent No. 4,105,578. Such clays are formed by the reaction of a methylbenzyl dialkyl ammonium compound,
35 wherein the ammonium compound contains 20 to 25% of alkyl groups having 16 carbon atoms and 60 to 75% of alkyl groups having

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18 carbon atoms, and a smectite-clay having a cationic exchange capacity of at least 75 millequivalents per hundred grams of clay, and wherein the amount of said ammonium compound is from 100 to 120 milliequivalents per hundred grams of clay, 100%

active clay basis. Non-limiting examples of such preferred organophilic clays include dimethyl dialkyl ammonium bentonite, dimethyl benzyl alkyl ammonium bentonite, methyl benzyl dialkyl ammonium bentonite, and mixtures thereof, wherein the alkyl group contains at least 12 carbon atoms, preferably 16 to 18 carbon atoms, and most preferably wherein the alkyl group is derived from hydrogenated tallow. An especially preferred organophilic clay is methyl benzyl dihydrogenated tallow ammonium bentonite.

When an organophilic clay is used as the compatibilizing agent, it is preferable to use a dispersant to enhance the dispersability of the organophilic clay in the oleaginous liquid. Generally speaking, the dispersant is a low molecular weight, polar organic compound such as an alcohol, ketone, or alkylene carbonate. Preferred are aliphatic alcohols having from 1 to 2 carbon atoms, ketones having from 2 to 5 carbon atoms, and mixtures thereof. Mixtures of such polar organic compounds and water can be used as well as water itself, the latter if sufficient shear is utilized to disperse the compatibilizing agent. A preferred dispersant comprises a methanol-water mixture containing from 75 to 98% by weight of methanol and from 25 to 2% by weight of water. The dispersant will be present in an amount of 1.5 to 100% by weight, based on the weight of the organophilic clay, more preferably from 20 to 40% by weight, based on the weight of the organophilic clay.

The compatibilizing agent will generally be present in the composition in amounts of from 0.25% to 3% by weight, based on the weight of the oleaginous liquid, preferably from 0.5 to 2% by weight, based on the weight of the oleaginous liquid.

The inorganic salt used in preparing the HEC compositions of this invention is any water soluble salt which has an exothermic heat of solution upon mixing the salt with water. The inorganic salt should be compatible

with the aqueous liquid to which the HEC composition is to be added. Preferred inorganic salts are calcium chloride, calcium bromide, zinc bromide, and mixtures thereof. Most preferably, the inorganic salt will be
5 calcium chloride, calcium bromide, or a mixture thereof. The inorganic salt should be present in an amount greater than 10% by weight of the aqueous phase (water plus inorganic salt), preferably greater than 20% by weight of the aqueous phase, up to a maximum concentration which
10 forms a saturated solution in the aqueous phase. Thus, for calcium chloride the maximum concentration is about 37% by weight and for calcium bromide about 55% by weight.

The concentration of water in the HEC composition of this invention will be such that the aqueous phase of
15 the composition generally comprises from 15 to 55% by weight of the composition, preferably from 25 to 45% by weight of the composition.

In preparing the liquid, polymer containing compositions, it is generally desirable to mix the compatibilizing agent and the oleaginous liquid followed by addition
20 of the dispersant under suitable mixing conditions until the desired viscosity is achieved. The aqueous phase is then added followed by the addition of the HEC. The composition is then thoroughly mixed, with shear, until
25 the desired viscosity is achieved. The water and inorganic salt are preferably added separately, the water being added first followed by addition of the inorganic salt. In this manner the exothermic heat of solution of the salt raises the temperature of the HEC composition,
30 preferably to a temperature greater than 65°C. If the water and inorganic salt are not added separately, then it is desirable to heat the HEC composition to a temperature of at least 65°C in order most satisfactorily to activate the HEC for use in heavy brines.

35 As noted, the compositions of the present invention can be mixed with aqueous systems to provide highly useful well drilling and treating fluids. While the aqueous

medium can comprise fresh water, preferably the aqueous medium will be one which contains a soluble salt, for example a soluble salt of an alkali metal, an alkaline earth metal, a Group IB metal, a Group IIB metal, ammonia or other anions. In particular, oil field brines containing sodium chloride and/or calcium chloride, when mixed with the compositions according to this invention make excellent workover fluids. The amount of the water soluble salt dissolved in the aqueous medium will vary depending upon the desired density of the well drilling or treating fluid. It is, however, common to employ saturated solutions of sodium chloride and/or calcium chloride in preparing such fluids. In preparing aqueous well drilling and treating fluids using the liquid, polymer-containing compositions, the amount of the liquid polymer composition added will vary depending upon the viscosity desired. Desirable well drilling and treating fluids can be made by combining an aqueous medium with sufficient composition according to this invention such that the final mixture contains from 2.5 to 6 g/l of HEC.

Another embodiment of this invention involves the use of the HEC composition of this invention to viscosify heavy brines having a density greater than 1.6 g/cm^3 . Such brines are particularly difficult, even if at all possible, to viscosify at ambient temperatures with HEC.

The heavy brines for use in the present invention contain two or more soluble salts selected from calcium chloride, calcium bromide, zinc bromide, and mixtures thereof. Brines containing only calcium chloride can be formulated having a density from 1.02 g/cm^3 . Brines containing only calcium bromide can be formulated having a density from 1.02 to 1.70 g/cm^3 . However, because calcium chloride is much less expensive than calcium bromide, brines in the density range from 1.35 to 1.81 g/cm^3 are generally formulated to contain both calcium chloride and calcium bromide, 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 brine will be used. Brines in the density range
5 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 bromide, and these brines are preferred for use in the
10 present invention. As indicated, such brines will have a density from 1.70 to 2.30 g/cm³.

Generally, brines of any density within the ranges disclosed are prepared by mixing together various standard, commercially available brines, as follows: calcium chloride
15 brines having a density in the range 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
20 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.

25 The brines which contain zinc bromide must contain at least 20% by weight of zinc bromide as disclosed in our prior British Patent Application No. 8131312 (publication No. 2108174 A).

The following non-limiting examples are presented
30 to illustrate the invention. Unless otherwise stated, all percentages are by weight.

Example 1

HEC compositions were prepared by the following procedure:

- (1) A stock mixture of diesel oil and methyl benzyl dihydrogenated tallow ammonium bentonite was prepared by mixing 300 grams of diesel oil with 30 grams of GELTONE II for 15 minutes on a Multimixer;
 - (2) The amount of this stock mixture indicated in Table 1 was added to the amount of diesel oil indicated in this table and mixed for 2 minutes on a Multimixer;
 - (3) The amount of a 95/5 (weight ratio) mixture of methanol and water indicated in Table 1 was added and mixed for 5 minutes on a Multimixer;
 - (4) The amount of water indicated in Table 1 was added and mixed 5 minutes on a Multimixer;
 - (5) The amount of 95% CaCl_2 indicated in Table 1 was added and mixed 2 minutes on a Multimixer; and
 - (6) The amount of NATROSOL 250 HHR hydroxyethyl cellulose indicated in Table 1 was added and mixed 20 minutes on a Multimixer.
- The samples were evaluated at a concentration of 2.85 g/l HEC in a 1.92 g/l $\text{CaBr}_2/\text{ZnBr}_2$ solution. The solutions were hand shaken for about 30 seconds, placed on a Fann VG rheometer at 300 rpm, and the dial reading taken after 1 and 2 hours, after rolling overnight at room temperature, and after rolling overnight at 65.5°C. The data obtained are given in Table 2.

Table 1

<u>Sample</u>	<u>A</u>	<u>B</u>	<u>C</u>
30 Diesel Oil	160	152.5	145
Stock Mixture	16.5	24.5	33
95/5 $\text{CH}_3\text{OH}/\text{H}_2\text{O}$	1.5	2.25	3
Water	102.6	102.6	102.6
95% CaCl_2	47.4	47.4	47.4
35 HEC	75	75	75

Table 2

<u>Sample</u>		<u>A</u>	<u>B</u>	<u>C</u>
	% HEC	18.6	18.5	18.5
	% Water	25.5	25.4	25.3
5	% CaCl_2 (95%)	11.8	11.7	11.7
	% Gelled Diesel Oil (GDO)	44.2	44.4	44.6
	% GELTONE II in GDO	0.84	1.25	1.66
<u>300 rpm Fann Dial Reading in 16.0 ppg Solution</u>				
10	g/cm^3 HEC	2.85	2.85	2.85
	Initial	10	10	10
	1 Hour	54	63	60
	2 Hours	64	73	70
	After Rolling at R.T.	64	70	70
15	After Rolling at 65.5°C	72	79	78

Example 2

HEC compositions were prepared by the following procedure:

(1) A stock mixture of diesel oil and methyl benzyl dihydrogenated tallow ammonium bentonite was prepared by mixing together with a Premier Dispersator for 20 minutes, 8000 parts by weight of diesel oil, 160 parts by weight of GELTONE II organophilic bentonite, and 45.5 parts by weight of a 95/5 (weight ratio) mixture of methanol and water, the latter functioning as a dispersion aid for the organophilic clay;

(2) To 150 gm of this gelled diesel oil were added 130.9 gm of water and this was mixed for two minutes on a Multimixer;

(3) 19.1 gm of 78% CaCl_2 were added and mixed three minutes;

(4) 75 gm of NATROSOL 250 HHR were added. Thickened immediately on mixing. An additional 50 gm of gelled diesel oil were added. Mixed 10 minutes on a Multimixer.
The product was designated Sample D.

(5) Sample E. Prepared as above except used 111.6 gm water, 38.4 gm of 78% CaCl_2 , and 25 gm of additional gelled diesel.

(6) Sample F. Prepared as (5) except used 92.3 gm of water and 57.7 gm of 78% CaCl_2 .

(7) Sample G. Prepared as (5) except used 73 gm of water and 77 gm of 78% CaCl_2 .

5 (8) Sample H. Prepared as (5) except that 102.7 gm of water and 47.3 gm of 95% CaCl_2 were used.

(9) Portions of samples D, E, F, and G were heated at 65.5°C overnight.

These samples were evaluated at a concentration of 2.85 g/l HEC in a 1.92 g/cm^3 $\text{CaBr}_2/\text{ZnBr}_2$ solution and/or a 2.30 g/cm^3 ZnBr_2 solution. The solutions were hand shaken for about 30 seconds, placed on a Fann VG rheometer at 300 rpm, and the dial readings taken periodically as indicated in Table 3.

15 The data obtained, given in Table 3, indicate that the CaCl_2 content of the aqueous phase should preferably be greater than about 20%. Heating the samples containing 10% and 20% CaCl_2 in the aqueous phase did not improve their rate of hydration in the 2.30 g/cm^3 brine.

20 Example 3

Sample I was prepared by adding 10 gm of NATROSOL 250 HHR to 20 gm of the gelled diesel oil of Example 2 and thereafter adding 20 gm of a 1.70 g/cm^3 CaBr_2 solution. Shaken by hand for mixing.

25 Sample J was prepared by mixing together 150 gm of gelled diesel oil and 62.6 gm of water with a Multimixer, adding 72.0 gm of 91% CaBr_2 , and adding 75 gm of HEC. Mixed with a Multimixer.

Sample K was prepared as Sample J except that the 30 water and CaBr_2 were mixed and cooled to room temperature being adding this solution to the gelled diesel oil, followed by the HEC.

Portions of samples J and K were heated at 65.5°C overnight.

35 The samples were evaluated in the same manner as in Example 3.

The data obtained, given in Table 4, indicate that

a good rate of hydration can be obtained in the 1.92 g/cm^3 brine and a fair rate of hydration in the 2.30 g/cm^3 brine, provided that the samples are prepared by the preferred process which utilizes dry inorganic salt rather than an
5 inorganic salt solution. The latter HEC composition, sample K, was inferior to sample J prepared using dry powder CaBr_2 . Heating sample K does increase the rate of hydration of the sample, however.

Table 3

Sample	D	E	F	G	H
% HEC	17.65	18.75	18.75	18.75	18.75
% Water	30.8	27.9	23.1	18.25	23.1
% CaCl ₂ (78%)	4.5	9.6	14.4	19.25	14.4
% Gelled Diesel Oil	47.05	43.75	43.75	43.75	43.75
Temperature, °C	49-65.5*	57-65.5*	65.5-65.5*	68-65.5*	77

300 rpm Fann Dial Reading in 1.92 g/cm³ Solution

g/cm ³ HEC	2.85	2.85	2.85	2.85	2.85
Initial	9	8	8	8	8
10 Minutes	12	11	16	18	17.5
20 Minutes	15	17	24	29	29.5
30 Minutes	18	23	32	40	39
1 Hour	23	38	54	59	60
2 Hours	-	-	-	-	69.5
After Rolling @ 65.5°C	70	68	70	72	74

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300 rpm Fann Dial Reading in 2.30 g/cm³ Solution

g/cm ³ HEC	2.85-2.85	2.85-2.85	2.85-2.85	2.85-2.85	2.85
Initial	21-22	21-22	21-22	21-22	22
10 Minutes	25--	24--	33--	36--	-
20 Minutes	30--	---	52--	50--	-
30 Minutes	36-27.5	43-36.5	74-76.5	71-81	80
1 Hour	48--	69--	108-110	109-114	116
2 Hours	---	---	---	---	124.5
24 Hours	---	---	---	---	-
After Rolling @ 65.5°C	128-107	123-128	127-129	126-133	128

* Sample rolled 20 hours @ 65.5°C

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Table 4

Sample	I	J	J	J	K	K
% HEC	20	20.85			20.85	
% Water	*	17.4			17.4	
% CaBr ₂ (91%)	*	20.0			20.0	
% Gelled Diesel Oil	40	41.75			41.75	
300 rpm Fann Dial Reading in 1.92 g/cm ³ Solution						
g/cm ³ HEC	2.85	2.85 (1)	2.85 (2)	2.85 (3)	2.85 (1)	2.85 (3)
Initial	8	8	8	8	8	8
10 Minutes	15	12.5	-	-	-	-
20 Minutes	24	20	-	-	-	-
30 Minutes	28	27.5	-	-	-	-
1 Hour	36	40	-	43	-	33
2 Hours	48	53.5	65	65	26	52
24 Hours	53	66	-	76	-	61
After Rolling at 65.5°C	69	76	77	75	67	60
300 rpm Fann Dial Reading in 2.30 g/cm ³ Solution						
g/cm ³ HEC	1	1	-	-	-	-
Initial	22	21.5	-	-	-	-
10 Minutes	24	27	-	-	-	-
20 Minutes	30	-	-	-	-	-
30 Minutes	37	55	-	-	-	-
1 Hour	76	86	-	-	-	-
2 Hours	-	-	-	-	-	-
24 Hours	-	130	-	-	-	-
After Rolling at 65.5°C	122	-	-	-	-	-

*Contains 40% of a 1.70 g/cm³ CaBr₂ solution. (1) Sample set for 16 hours before testing.
 (2) Sample set for several days testing. (3) Sample heated at 65.5°C overnight before testing.



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CLAIMS

1. A viscosifying composition which will hydrate in and viscosify heavy brines having a density greater than 1.6 g/cm^3 at ambient temperatures which comprises an oleaginous liquid, an aqueous phase comprising
5 water and an inorganic salt which has an exothermic heat of solution the concentration of inorganic salt being greater than 10% by weight of the aqueous phase, and a compatibilizing agent, and hydroxyethyl cellulose.

2. A composition as claimed in claim 1 which
10 comprises
from 10 to 30% by weight of hydroxyethyl cellulose,
from 35 to 55% by weight of the oleaginous liquid,
from 15 to 55% by weight of the aqueous phase comprising water and the inorganic salt, and
15 from 0.25 to 3% by weight, based on oleaginous liquid, of the compatibilizing agent.

3. A composition as claimed in claim 1 or 2 which comprises
from 15 to 25% by weight of hydroxyethyl cellulose,
from 40 to 50% by weight of the oleaginous liquid,
20 from 25 to 45% by weight of the aqueous phase comprising water and the inorganic salt, wherein the concentration of inorganic salt is greater than 20% by weight of the aqueous phase, and

from 0.5 to 2% by weight, based on oleaginous liquid of
25 the compatibilizing agent.

4. A composition as claimed in any preceding claim wherein the oleaginous liquid is an aliphatic or aromatic hydrocarbon having 5 to 10 carbon atoms, diesel oil, kerosene, a petroleum distillate or a petroleum oil.

5. A composition as claimed in any preceding claim wherein
30 the compatibilizing agent is an organophilic hectorite, an organophilic attapulgite, an organophilic sepiolite, fumed silica, surface-treated



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5 silica or an organophilic clay obtained by reacting a methyl benzyl dialkyl ammonium compound containing 20 to 25% of C₁₆ alkyl groups and 60 to 75% of C₁₈ alkyl groups, with a smectite clay having a cation-exchange capacity of at least 75 milliequivalents per 100 g of clay, the amount of ammonium compound being from 100 to 120 milliequivalents per 100 g of clay.

10 6. A composition as claimed in any preceding claim wherein the inorganic salt having an exothermic heat of solution is calcium chloride, calcium bromide, zinc bromide or a mixture thereof.

7. A composition as claimed in any preceding claim which has been heated to a temperature of at least 65°C.

15 8. A composition as claimed in claim 7 wherein the temperature results from the solution of the inorganic salt in the water.

20 9. A composition as claimed in claim 1 and substantially as hereinbefore described with reference to any of the Examples.

25 10. A method of activating hydroxyethyl cellulose such that said hydroxyethyl cellulose will hydrate in heavy brines having a density greater than 1.6 g/cm³ at ambient temperatures which comprises mixing an oleaginous liquid and a compatibilizing agent together to form a viscous slurry, mixing the slurry with an aqueous phase comprising water and an inorganic salt which has an exothermic heat of

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solution the concentration of inorganic salt being greater than 10% by weight of the aqueous phase, and then with hydroxyethyl cellulose to form a viscous pourable composition.





11. A method as claimed in Claim 10 wherein the aqueous solution is added in two separate parts, first water followed by the inorganic salt.

12. A method as claimed in Claim 10 or 11 wherein
5 the viscous pourable composition contains
from 10 to 30% by weight of hydroxyethyl cellulose,
from 35 to 55% by weight of the oleaginous liquid,
from 15 to 55% by weight of an aqueous phase com-
prising water and the inorganic salt, wherein the concen-
10 tration of inorganic salt is greater than 10% by weight
of the aqueous phase, and
from 0.25 to 3% by weight, based on oleaginous
liquid, of the compatibilizing agent.

13. A method as claimed in any of Claims 10 to 12
15 wherein the viscous pourable composition contains
from 15 to 25% by weight of hydroxyethyl cellulose,
from 40 to 50% by weight of the oleaginous liquid,
from 25 to 45% by weight of an aqueous phase com-
prising water and the inorganic salt, wherein the concen-
20 tration of inorganic salt is greater than 20% by weight
of the aqueous phase, and
from 0.5 to 2% by weight, based on oleaginous
liquid of the compatibilizing agent.

14. A method as claimed in any of Claims 10 to 13
25 wherein the oleaginous liquid is an aliphatic or aromatic
hydrocarbon having 5 to 10 carbon atoms, diesel oil,
kerosene, a petroleum distillate or a petroleum oil.

15. A method as claimed in any of Claims 10 to 14
wherein the compatibilizing agent is an organophilic hec-
30 torite, an organophilic attapulgite, an organophilic
sepiolite, fumed silica, surface treated silica or an
organophilic clay obtained by reacting a methylbenzyl
dialkyl ammonium compound containing 20 to 25% of C₁₆
alkyl groups and 60 to 75% of C₁₈ alkyl groups, with a



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smectite clay having a cation-exchange capacity of at least 75 milliequivalents per 100 g of clay, the amount of ammonium compound being from 100 to 120 milliequivalents per 100 g of clay.

5 16. A method as claimed in any of Claims 10 to 15 wherein the inorganic salt having an exothermic heat of solution is calcium chloride, calcium bromide, zinc bromide or a mixture thereof.

10 17. A method as claimed in any of Claims 10 to 16 which additionally comprises heating the viscous pourable composition to a temperature of at least 65°C.

18. A method as claimed in Claim 17 wherein the temperature results from the solution of the inorganic salt in the water.

15 19. A method as claimed in Claim 10 and substantially as hereinbefore described with reference to any of the Examples.

20 20. Activated hydroxyethyl cellulose compositions when obtained by a method as claimed in any of Claims 10 to 19.

25 21. A well servicing fluid which comprises a heavy brine having a density greater than 1.6 g/cm³ containing a soluble salt selected from calcium chloride, calcium bromide, zinc bromide, and mixtures thereof, and a viscosifying amount of a composition as claimed in any of Claims 1 to 9 and 20.
