

AQUEOUS WELL SERVICING FLUIDS

The present invention relates to a method and composition for increasing the viscosity and reducing the fluid loss of aqueous systems used as well servicing fluids.

Aqueous mediums, 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, etc. Such well servicing fluids, if they are to be effective and economically attractive, must exhibit low fluid loss. It is known to add to the well servicing fluid certain hydrophilic polymeric materials for fluid loss control. For example, it is known to use starch and cellulose products, e.g. corn starch and potato starch derivatives, as additives to well servicing fluids for fluid loss control. The degree of fluid loss control exhibited by such materials is largely dependent upon the composition of the well servicing fluid. Thus, it is known that the presence of high concentrations of calcium or zinc ions, common components of heavy brines, makes fluid loss control more difficult.

Viscosity enhancement of aqueous well servicing fluids is also necessary in many applications. Again, starch and cellulose derivatives have been used to achieve such viscosity enhancement, but their effectiveness is also affected by the presence, in certain heavy brines, of high concentrations of calcium or zinc ions.

It is, therefore, an object of the present invention to provide a new composition for synergistically increasing the viscosity and controlling the fluid loss of aqueous well servicing fluids.

A further object of the present invention is to provide a new composition useful for synergistically increasing the viscosity and lowering the fluid loss of aqueous brine

solutions used as well servicing fluids.

Still a further object of the present invention is to provide an improved method for decreasing the fluid loss of an aqueous well servicing fluid.

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

10 In accordance with one embodiment of the present invention, there is provided a method for decreasing the fluid loss of an aqueous well servicing fluid by adding and dispersing in the well servicing fluid an effective amount of a cross-linked hydroxyethyl starch and an effective amount of a hydroxyethyl cellulose.

15 In another embodiment of the present invention, there is provided a composition useful for increasing the viscosity and lowering the fluid loss of an aqueous medium comprised of a cross-linked hydroxyethyl starch and a hydroxyethyl cellulose.

20 In yet another embodiment of the present invention, there is provided a well servicing fluid comprised of an aqueous medium, an effective amount of a cross-linked hydroxyethyl starch and an effective amount of a hydroxyethyl cellulose.

25 The two polymeric components of the novel composition of the present invention are cross-linked hydroxyethyl starch and hydroxyethyl cellulose (HEC). The HEC polymers are generally 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

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degree of substitution, the greater the water solubility. It is preferable to use HEC polymers having as high a mole substitution level as possible.

The HEC polymers which are useful in the present invention, depending upon the method of preparation of the well servicing fluids, can either be in the form of a dry powder, essentially untreated, or can be an "activated" HEC. The term "activated" as used herein refers to an HEC polymer which will substantially hydrate or solubilize in a brine solution having a density greater than 1.701 g/ml without the necessity for mixing, as by rolling, at elevated temperatures. Examples of such activated HEC polymers are to be found in British Patent Applications Nos. 8101828 and 8109880. As disclosed in the aforementioned Patent Applications, HEC polymers which have been activated will solubilize in brine solutions without the necessity for rolling or other forms of mixing at elevated temperatures. In general, any HEC polymer which will solubilize in a brine having a density in excess of 1.701 g/ml at room temperature can be considered an "activated" HEC. It is to be understood, however, that the present invention is not limited to the use of such activated HEC polymers. Depending upon the condition of mixing, and the composition of the aqueous well servicing fluid, unactivated or dry powder HEC polymers are compatible with the aqueous well servicing fluids used in the present invention. The term "compatible" as used herein, means that the HEC polymer can be solvated or solubilized in a given aqueous solution with the use of mixing techniques such as rolling at elevated temperatures. Thus, an incompatible system is one in which the HEC polymer will not solubilize in the brine regardless of the mixing conditions used.

The other polymeric component of the compositions of the present invention is a cross-linked hydroxyethyl starch. Such hydroxyethyl starches are produced by introduction of non-ionic hydroxyethyl side groups onto the

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onto the polymer chain of the starch followed by cross-linking techniques well known in the art such as, for example, those disclosed in U.S. Patents Nos. 2,500,950; 2,929,811; 2,989,521 and 3,014,901. Generally speaking, the cross-linked hydroxyethyl starches which are useful in the present invention are those in which the hydroxyethyl side chain degree of substitution (DS) is from 0.15 to 0.8, preferably from 0.25 to 0.6. A particularly useful cross-linked hydroxyethyl starch is known as BOHRAMYL CR, a cross-linked potato starch derivative manufactured by Avebe (Veendam, Holland). BOHRAMYL CR, which is a coarse white flaky material, has a bulk density (kg/m^3) of approximately 325 and a DS of about 0.4.

As noted above with respect to the HEC, the cross-linked hydroxyethyl starch may be utilized either in the form of a dry powder or flake, essentially untreated, or can be an "activated" starch, wherein the term "activated" has the same meaning as used above with respect to the discussion of activated HEC. Methods of activating the cross-linked hydroxyethyl starch are disclosed in British Patent Application No. 8101828. It is to be understood that the present invention is not limited to the use of activated hydroxyethyl starch. Indeed, it is a feature of the present invention that both the HEC and the hydroxyethyl starch can be used in dry form to produce well servicing fluids which exhibit excellent rheological properties and low fluid loss. However, in certain brine solutions, activation or presolvation of the HEC and/or the hydroxyethyl starch may be desirable to reduce mixing times and severity of conditions of mixing.

The polymer composition of the present invention which can be used to decrease fluid loss and increase the viscosity of aqueous well servicing fluids is comprised of an effective amount of HEC and an effective amount of the cross-linked hydroxyethyl starch. It has been found that when these two polymeric materials are added to aqueous well servicing fluids, depending upon the nature of the fluid,

synergistic enhancement of viscosity and/or fluid loss is achieved. The particular amount of each of the polymeric components present in the additive composition will vary depending upon the nature and composition of the aqueous

5 well servicing fluid with which the additive is to be admixed. In general, the polymer composition of the present invention will contain a weight ratio of hydroxyethyl starch to HEC of from 10 to 90 to 90 to 10, preferably from 33 to 67 to 75 to 25. The polymeric composition of the present
10 invention can be either in the form of a dry mixture of the HEC and the hydroxyethyl starch or, if preferred, it can be in the form of solvated or activated forms of the polymers. Thus, for example, the HEC and the hydroxyethyl starch can be activated and those activated solutions mixed together
15 to provide the novel polymeric compositions used herein.

The novel well servicing fluid of the present invention comprises an aqueous medium and an effective amount of a cross-linked hydroxyethyl starch and an effective amount of a hydroxyethyl cellulose. The relative amounts of
20 the hydroxyethyl starch and the HEC admixed with the aqueous medium is such as to provide a synergistic decrease in the fluid loss of the aqueous medium. Again, the precise amount of each of the polymeric components used will depend upon the nature of the aqueous well servicing fluid.

25 In general, however, the weight ratio of the hydroxyethyl starch to the HEC in the well servicing fluid will be from 10 to 90 to 90 to 10, more preferably from 33 to 67 to 75 to 25.

30 In general, the well servicing fluids will contain the polymer components in amounts of from 0.7 to 14.3 g/l HEC and from 1.4 to 14.3 g/l hydroxyethyl starch.

The aqueous medium used in the well servicing fluids of the present invention can range from fresh water to heavy brines having a density in excess of 2.277 g/ml.
35 Generally speaking, well servicing fluids as, for example, those used in completion and workover operations, are made from aqueous mediums containing soluble salts such as, for

example, a soluble salt of an alkali metal, an alkali earth metal, a Group Ib metal, a Group IIb metal, as well as water soluble salts of ammonia and other cations. The mixed HEC/cross-linked hydroxyethyl starch compositions are particularly useful in the preparation of low fluid loss, heavy brines, i.e. aqueous solutions of soluble salts of multivalent ions, e.g. Zn and Ca.

The preferred heavy brines useful in forming the well servicing fluids of the present invention are those having a density greater than 1.318 g/ml, preferably those having a density of more than 1.4 g/ml, and especially those having a density greater than 1.797 g/ml. The method of the invention can, for example, be used for aqueous media having a density from 1.438 to 2.301 g/ml. Such heavy brines are comprised of water solutions of salts selected from the group consisting of calcium chloride, calcium bromide, zinc chloride, zinc bromide, and mixtures thereof.

We have shown in co-pending patent application No. 8131312, that in certain heavy brines containing zinc bromide in a concentration of less than 20% by weight, HEC is incompatible, i.e. it will not solvate in such brines to efficiently enhance the viscosity. However, according to the present invention, by adding the synergistic combination of HEC and the cross-linked hydroxyethyl starch, brine solutions wherein the content of zinc bromide is from 0.5 to 20% by weight, and the density is from 1.438 to 2.301 g/ml can be viscosified.

If desired, bridging agents may be added to the well servicing fluids to aid in fluid loss control. Indeed, somewhat lower filtrates are obtained with their use. However, it is a distinct and unexpected feature of the invention that a bridging agent is not necessary to achieve low fluid loss values in aqueous brines. Thus, using the present invention, it is possible to obtain clear, heavy brines having low fluid loss characteristics and, at low concentrations of HEC, having low rheological characteristics.

In the method of the present invention, the mixed HEC/cross-lined hydroxyethyl starch can be added to the aqueous well servicing medium either in the dry form or in the activated form as discussed above. In the method, the polymeric components are dispersed in the aqueous medium by suitable mixing techniques.

To more fully illustrate the present invention, the following non-limiting examples are presented. Unless otherwise indicated, all physical property measurements were made in accordance with testing procedures set forth in STANDARD PROCEDURE FOR TESTING DRILLING MUD API RP 13B, Seventh Edition, April, 1978. The HEC polymer employed, unless otherwise indicated, was an HEC marketed by Hercules, Inc., under the trade-name NATROSOL 250 HHR. The cross-linked hydroxyethyl starch employed, unless otherwise indicated, was BOHRAMYL CR marketed by Avebe (Veendam, Holland).

NATROLSOL, CAB-O-SIL and KLUCEL are Registered Trade Marks.

Example 1

To show the effect on viscosity and fluid loss achieved by mixing HEC and cross-linked hydroxyethyl starch, 5.7 g/l of HEC and either 0, 5.7 or 11.4 g/l of BOHRAMYL CR were added to an aqueous brine containing 85.58 g/l calcium chloride and mixed for 30 minutes on a Multimixer. Thereafter, the samples were rolled at 65.6°C for 16 hours, cooled, stirred for 5 minutes and the API rheology and fluid loss determined. The data obtained and given in Table 1 below indicate that the BOHRAMYL CR efficiently decreased the fluid loss in the brine in the presence of HEC.

Table 1

	<u>API Properties</u>	<u>g/l BOHRAMYL CR</u>		
		<u>0</u>	<u>5.7</u>	<u>11.4</u>
15	Apparent Viscosity, cp	40	57	82
	Plastic Viscosity, cp	20	25	32
	Yield Point, Kg/m ²	1.95	3.17	4.93
	10 Sec. Gel Strength, Kg/m ²	0.15	0.34	0.59
	pH	7.6	7.8	7.8
20	API Fluid Loss	50	14.2	7.3

Example 2

The example demonstrates the use of using solvated HEC compositions. The following samples were prepared:

Sample A

124.5 parts of isopropanol and 0.5 parts of CAB-O-SIL M5 (colloidal silica) were mixed 10 minutes on a Multimixer. There was then added 50 parts by weight of HEC and mixing continued for an additional 3 minutes. Following this, 75 parts by weight of ethylene glycol were added and an additional 5 minutes of mixing conducted.

Sample B

A solution of 0.5% by weight Klucel H (hydroxypropyl cellulose) in isopropanol was prepared. To 55 parts by weight of this isopropanol solution were added 20 parts by weight of HEC and 25 parts by weight of ethylene glycol.

The brine solution used to evaluate the samples was

a 1.917 g/ml $\text{CaBr}_2/\text{ZnBr}_2$ solution. The brine samples were prepared and evaluated using the following procedure:

1. The amounts of HEC, BOHRAMYL CR and BARACARB (CaCO_3 bridging agent) indicated in Tables 2, 3 and 4 were added to the 1.917 g/ml brine and mixed on a Multimixer for 15 minutes.

2. The API rheology was then obtained.

3. The samples were then aged overnight at room temperature and the API rheology and fluid loss obtained.

10 4. The samples were then rolled overnight at 65.5°C and the API rheology and fluid loss obtained after the samples had cooled to room temperature.

Table 2 gives the data obtained using Sample A.

Table 3 gives the data obtained using Sample B. Table 4
15 gives the data obtained for BOHRAMYL CR alone.

Table 2

Effect of BOHRAMYL CR on the Properties of a 1.917 g/ml $\text{CaBr}_2/\text{ZnBr}_2$
Solution Viscosified with NATROSOL 250HHR Hydroxyethyl Cellulose

	1	2	3	4	5	6	7	8	9
NATROSOL 250HHR, g/l*	2.85	2.85	2.85	2.85	5.7	5.7	5.7	5.7	2.85**
BOHRAMYL CR, g/l	0	2.85	5.7	8.56	0	2.85	5.7	8.56	8.56

Initial Properties After 15 Minutes on a Multimeter

A.V. 1	18	35	37	26.5	52.5	54	60	75.5	43
P.V. 2	16	32	35	21	33	35	36	36	28
Y.P. 3	0.20	0.29	0.20	0.54	1.90	1.90	1.90	3.86	1.46
10-Sec. Gel Str. 4	0.05	0.05	0.05	0.05	0.20	0.20	0.24	0.49	0.15

Properties After Hydrating Overnight at 23.3°C

A.V.	36	50	60	67	93.5	105	122	OS	68
P.V.	25	32	38	41	49	57	63	OS	40
Y.P.	1.07	1.76	2.15	2.54	4.34	4.69	5.81	OS	2.73
10-Sec. Gel Str.	0.10	0.20	0.29	0.34	1.03	1.17	1.56	2.49	0.29
API Fluid Loss	162	25	8	6.8	120	18	10	1.6	1.8

Properties After Rolling Overnight at 65.5°C

A.V.	51	65.5	79	96	113	139	OS	OS	81
P.V.	32	40	49	59	56	68	OS	OS	45
Y.P.	1.86	2.49	2.93	3.61	5.57	6.98	OS	OS	3.52
10-Sec. Gel Str.	0.29	0.39	0.54	0.78	1.51	2.15	2.59	3.08	0.44
API Fluid Loss	NC	23	10.5	6.0	205	20	6	3	1.4

Effect of BOHRAMYL CR on the Properties of a 1.917 g/ml $\text{CaBr}_2/\text{ZnBr}_2$
Solution Viscosified with NATROSOL 250HHR Hydroxyethyl Cellulose

Table 2 (Cont'd)

* Added as 14.265 g/l of a sample containing 20% HEC, 30% Ethylene Glycol, 49.8% Isopropanol, and 0.2% CAB-O-SIL M5.

** Added as 14.265 g/l of a sample containing 20% HEC, 25% Ethylene Glycol, 54.7% Isopropanol, and 0.3% KLUCEL H (hydropropyl cellulose).

1 Apparent Viscosity (cp).

2 Plastic Viscosity (cp).

3 Yield Point (Kg/m^2).

4 Kg/m^2 .

Table 3

Effect of BOHRAMYL CR on the Properties of a 1.917 g/ml
CaBr₂/ZnBr₂ Solution Viscosified with NATROSOL 250HR
Hydroxyethyl Cellulose and Containing a Bridging Agent

	10	11	12	13	14	15	16	17	18
NATROSOL 250HR, g/l*	2.85	2.85	2.85	2.85	5.7	5.7	5.7	5.7	2.85**
BOHRAMYL CR, g/l	0	2.85	5.7	8.56	0	2.85	5.7	8.56	8.56
BARACARB, g/l	8.56	8.56	8.56	8.56	8.56	8.56	8.56	8.56	8.56

Initial Properties After 15 Minutes on a Multimixer

A.V.	18.5	34.5	37.5	27.5	54.5	51.5	73.5	75.5	41
P.V.	16	32	32	22	33	33	38	36	26
Y.P.	0.24	0.24	0.54	0.54	2.10	1.81	3.47	3.86	1.46
10-Sec. Gel Str.	0.05	0.05	0.10	0.05	0.24	0.20	0.44	0.49	3

Properties After Hydrating Overnight at 23.3°C

A.V.	36	49.5	60	67.5	95	95	131	OS	68
P.V.	25	33	35	41	49	51	65	OS	40
Y.P.	1.07	1.66	2.44	2.59	4.49	4.30	6.44	OS	2.73
10-Sec. Gel Str.	0.10	0.20	0.29	0.34	1.03	0.98	1.76	2.49	0.29
API Fluid Loss	10	7.8	10	6.4	9.6	18	5	1.6	1.8

Properties After Rolling Overnight at 65.5°C

A.V.	54	65	80.5	95.5	122	127	OS	OS	80.5
P.V.	34	40	49	57	59	65	OS	OS	45
Y.P.	1.95	2.44	3.08	3.76	6.15	6.10	OS	OS	3.47
10-Sec. Gel Str.	0.29	0.39	0.54	0.78	1.76	1.76	2.54	3.03	0.44
API Fluid Loss	18.5	16.5	7.5	5.0	36.2	13	3	3	1.4

Table 3 (Cont'd)

Effect of BOHRAMYL CR on the Properties of a 1.917 g/ml
CaBr₂/ZnBr₂ Solution Viscosified with NATROSOL 250HHR
Hydroxyethyl Cellulose and Containing a Bridging Agent

* Added as 14.265 g/l of a sample containing 20% HEC, 30% Ethylene Glycol, 49.8% Isopropanol, and 0.2% CAB-O-SIL M5 (HEC-1).

** Added as 14.265 g/l of a sample containing 20% HEC, 25% Ethylene Glycol, 54.7% Isopropanol, and 0.3% KLUCEL H (HEC-2).

Table 4

Effect of BOHRAMYL CR on the Properties of a 1.917 g/ml
CaBr₂/ZnBr₂ Solution

	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>	<u>24</u>	<u>25</u>
BOHRAMYL CR, g/l	2.85	5.7	8.56	11.4	2.85	5.7	8.56
BARACARB CaCO ₃ , g/l	0	0	0	0	8.56	8.56	8.56

Initial Properties After 15 Minutes on a Multimixer

A.V.	6.5	6.5	7	-	6.5	6.5	7
P.V.	7	6	7	-	7	6	7
Y.P.	-0.05	0.05	0	-	-0.05	0.05	0
10-Sec. Gel Str.	0	0	0	-	0	0	0

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Properties After Hydrating Overnight at 23.3°C

A.V.	10	13	18	20.5	10	13	18.5
P.V.	10	13	18	20	10	13	18
Y.P.	0	0	0	0.5	0	0	0.05
10-Sec. Gel Str.	0	0	0	0.5	0	0	0.05
API Fluid Loss	89	68	28	10.8	57	20	13

Properties After Rolling Overnight at 65.5°C

A.V.	10	13.5	19	23.5	10	13.5	20
P.V.	10	14	19	23	10	14	20
Y.P.	0	-0.05	0	0.05	0	-0.05	0
10-Sec. Gel Str.	0	0	0	0	0	0	0.05
API Fluid Loss	107	61	30	20	50	35	15

The data obtained and shown in Tables 2, 3 and 4 indicate that the HEC and the BOHRAMYL CR combine to synergistically increase the viscosity and decrease the fluid loss of the aqueous brine. The fluid loss results in the absence of the BARACARB bridging agent are particularly outstanding. The aqueous brines, after hot rolling, were completely clear as all of the polymers were dissolved.

Example 3

To demonstrate the effect of HEC and BOHRAMYL CR on heavy brines containing less than 20% by weight ZnBr_2 , the following procedure was carried out: a 1.833 g/ml $\text{CaBr}_2/\text{ZnBr}_2$ solution containing 15.7% ZnBr_2 and 43.9% CaBr_2 was prepared by mixing together a 2.301 g/ml solution containing 57% by weight ZnBr_2 , and 20% by weight CaBr_2 and a 1.702 g/ml solution containing 53% by weight CaBr_2 in a volume ratio of 0.78/0.22, respectively. To three separate portions of this brine solution were mixed, on a Multimixer for 15 minutes, the following:

1. 8.56 g/l BOHRAMYL CR
2. 2.85 g/l HEC
3. 8.56 g/l BOHRAMYL CR and 2.85 g/l HEC.

The Fann V-G meter viscosities were then obtained, and after rolling the solutions for 3 hours and overnight at 65.5°C. The data obtained are given in Table 5.

Table 5

BOHRAMYL CR, g/l	8.56	8.56	0
NATROSOL 250HHR, g/l	0	2.85	2.85

Fann V-G Rheology

5 After 15 Minutes Mixing

Apparent Viscosity	7.5	8	*
Plastic Viscosity	7.5	7.5	*
Yield Point	0	0.05	*
10-Sec. Gel Str.	0	0	*

10 After Rolling 3 Hours at 65.5°C

Apparent Viscosity	13.5	20	*
Plastic Viscosity	13.5	19	*
Yield Point	0	0.10	*
10-Sec. Gel Str.	0.05	0.05	*

15 After Rolling Overnight at 65.5°C

Apparent Viscosity	14	23.5	**
Plastic Viscosity	14	22	**
Yield Point	0	0.15	**
10-Sec. Gel Str.	0.02	0.05	**

20 * No HEC hydration and dispersion.

** Large hydrated lumps on top of solution.

The data clearly indicate the synergistic results obtained on adding both the BOHRAMYL CR and HEC to the brine. Indeed, it was noted that the HEC would not hydrate and disperse in the brine when added without the BOHRAMYL CR.

Example 4

In this example two samples of non-cross-linked hydroxyethyl starch were evaluated and compared with BOHRAMYL CR. The HEC sample used was Sample A of Example 2. The samples were evaluated as per the procedure given in Example 2. The two non-cross-linked hydroxyethyl starches

had hydroxyethyl degrees of substitution of 0.29 and 0.83. The data, given in Table 6, clearly indicate that the hydroxyethyl starch must be cross-linked in order to interact with the HEC to synergistically decrease the fluid loss

5 of the brine.

Table 6

HEC, g/l	2.85	0	2.85	0	2.85	0	2.85
HES ¹ , 0.29 DS, g/l	0	5.7	5.7	0	0	0	0
HES, 0.83 DS, g/l	0	0	0	5.7	5.7	0	0
BOHRAMYL CR, g/l	0	0	0	0	0	5.7	5.7

Initial Properties After 15 Minutes on a Multimixer

Apparent Viscosity	22	8	22	9	23	8	26
Plastic Viscosity	19	8	19	9	20	8	21
Yield Point	0.34	0	0.34	0	0.29	0	0.54
10-Sec. Gel Str.	0.05	0.05	0.05	0.05	0.05	0	0.05

Properties After Hydrating Overnight at 23.3°C

Apparent Viscosity	42	12	43	12	45	10	50
Plastic Viscosity	29	12	33	12	31	10	33
Yield Point	1.32	0	1.03	0	1.42	0	1.66
10-Sec. Gel Str.	0.20	0.05	0.15	0.05	0.20	0	0.20
Fluid Loss	42	19	22	21	90	15	15

Properties After Rolling Overnight at 65.5°C

Apparent Viscosity	55	19	73	11	57	13	77
Plastic Viscosity	35	19	47	11	37	13	37
Yield Point	2.00	0	2.59	0	1.95	0	3.95
10-Sec. Gel Str.	0.29	1	0.39	0	0.24	0	0.49
Fluid Loss	60	11	80	35	158	10	3

¹ Non-cross-linked hydroxyethyl starch.

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Example 5

This example demonstrates the synergistic effect on viscosity and fluid loss in fresh water and in lower density brine solutions (1.390 g/ml CaCl_2). The samples used were
5 prepared as follows:

1.390 g/ml Brine

The indicated amounts of BOHRAMYL CR and HEC were added to the brine and mixed for 15 minutes on a Multimixer. After obtaining the API viscosities, the samples were rolled
10 at 65.5°C for 16 hours, cooled to 23.3°C, and the API viscosities and API fluid loss obtained.

Tap Water

These samples were prepared and evaluated as in the case of the brine with the exception that 1 g/l of magnesium
15 oxide were added to each sample to raise the pH and decrease the hydration time of the HEC.

The data, shown in Table 7, clearly indicate synergistic increase in both viscosity and fluid loss on the fresh water and the brine.

Example 6

This example compares the effect of cross-linked hydroxyethyl starch and non-cross-linked hydroxyethyl starch in combination with HEC in a 10% NaCl solution. The indicated amounts of HEC and the hydroxyethyl starch were added to separate 350 ml portions of a 10% NaCl solution. Rheological data obtained after 25 minutes of mixing and after rolling at 65.5°C, cooling at 23.3°C and mixing for an additional 5 minutes are shown in Table 8. As the data in Table 8 clearly show, cross-linked hydroxyethyl starch in admixture with HEC synergistically interacts to decrease the fluid loss and increase the viscosity. However, samples of hydroxyethyl starch which are not cross-linked only synergistically interact with the HEC to increase the viscosity.

Table 8

After 25 Minutes Mixing

After Rolling @ 65.5°C, Cooling to 23.3°C, and Mixing 5

1 Hydroxyethyl starch.

* NC = No Control.



CLAIMS:

1. A method of decreasing the fluid loss of aqueous well servicing fluids which comprises dispersing in said fluid an effective amount of a cross-linked hydroxyethyl starch and an effective amount of a hydroxyethyl cellulose,
5 the relative amounts of said hydroxyethyl starch and said hydroxyethyl cellulose being such as to decrease synergistically the fluid loss of said aqueous fluid.
2. A method as claimed in claim 1 wherein the
10 aqueous fluid comprises an aqueous solution of at least one water soluble salt of a multi-valent metal ion.
3. A method as claimed in claim 2 wherein the water soluble salt is calcium chloride, calcium bromide, zinc chloride, zinc bromide, or a mixture thereof.
- 15 4. A method as claimed in any preceding claim wherein the aqueous medium has a density greater than 1.4 g/ml.
5. A method as claimed in any preceding claim wherein the density of the aqueous medium is from 1.438 to
20 2.301 g/ml.
6. A method as claimed in claim 2 wherein the aqueous medium contains from 0.5 to 20% by weight of zinc bromide and has a density in the range of from 1.701 to 1.947 g/ml.
7. A method as claimed in any preceding claim
25 wherein the weight ratio of hydroxyethyl starch to hydroxyethyl cellulose is from 10 to 90 to 90 to 10.
8. A method as claimed in claim 7 wherein the weight ratio is from 33 to 67 to 75 to 25.



9. A method as claimed in any preceding claim wherein the hydroxyethyl starch and hydroxyethyl cellulose are activated before being dispersed in the aqueous fluid.
- 5 10. A composition for increasing the viscosity and decreasing the fluid loss of aqueous well servicing fluids which comprises a mixture of a cross-linked hydroxyethyl starch and a hydroxyethyl cellulose, the relative amounts of hydroxyethyl starch and hydroxyethyl cellulose being such as
10 to decrease synergistically the fluid loss from the aqueous fluid.
11. A composition as claimed in claim 10 wherein the weight ratio of hydroxyethyl starch to hydroxyethyl cellulose is from 10 to 90 to 90 to 10.
- 15 12. A composition as claimed in claim 11 wherein the ratio is from 33 to 67 to 75 to 25.
13. A composition as claimed in any of claims 10 to 12 wherein the hydroxyethyl starch and hydroxyethyl cellulose are activated.
- 20 14. A well servicing fluid which comprises:
 an aqueous medium; and
 an effective amount of a cross-linked hydroxyethyl starch and an effective amount of a hydroxyethyl cellulose, the relative amounts of hydroxyethyl starch and hydroxyethyl
25 cellulose being such as to decrease synergistically the fluid loss of the aqueous medium.
15. A composition as claimed in claim 14 wherein the aqueous medium comprises a solution of at least one water soluble salt of a multi-valent metal ion.
- 30 16. A composition as claimed in claim 15 wherein the water soluble salt is calcium chloride, calcium bromide, zinc chloride, zinc bromide, or a mixture thereof.

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17. A composition as claimed in any of claims 14 to 16 wherein the aqueous medium has a density greater than 1.4 g/ml.

5 18. A composition as claimed in any of claims 14 to 17 wherein the density of the aqueous medium is from 1.438 to 2.301 g/ml.

10 19. A composition as claimed in claim 15 wherein the aqueous medium contains from 0.5 to 20% by weight of zinc bromide and has a density in the range from 1.701 to 1.947 g/ml.

20. A composition as claimed in any of claims 14 to 19 wherein the hydroxyethyl starch and hydroxyethyl cellulose are activated.

15 21. A composition as claimed in any of claims 14 to 20 wherein the weight ratio of hydroxyethyl starch to hydroxyethyl cellulose is from 10 to 90 to 90 to 10.

22. A composition as claimed in claim 21 wherein the ratio is from 33 to 67 to 75 to 25.

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

24. A composition as claimed in claim 14 and substantially as hereinbefore described with reference to any of the Examples.