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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
5 field brines, are commonly used as well servicing fluids such as drilling fluids, workover fluids, completion fluids, packer 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
10 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, e.g. brines, for fluid loss
15 control.

Viscosity enhancement of aqueous well servicing fluids, e.g. brines, is also necessary in many applications. Again, starch and cellulose derivatives have been used to achieve such viscosity enhancement.

20 Examples of prior art which discloses various additives to well servicing fluids for viscosity enhancement and/or fluid loss control include U.S. Patent 3,625,889 which teaches a well completion fluid consisting of aqueous calcium chloride, carboxymethyl cellulose (CMC) and xanthan gum (XC
25 polymer), and U.S. Patent 3,953,336 which discloses mixtures of XC polymer with various cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose, etc.

It is, therefore, an object of the present invention to provide a new composition for synergistically increasing
30 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 increas-

ing 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
5 an aqueous well servicing fluid.

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

In accordance with one embodiment of the present
10 invention, there is provided a method for decreasing the fluid loss of an aqueous well servicing fluid comprising adding and dispersing in the well servicing fluid an effective amount of a cross-linked hydroxyethyl starch (HES) and an effective amount of a material selected from the class
15 consisting of carboxymethyl cellulose ethers, XC polymer and mixtures thereof.

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 com-
20 prised of an effective amount of a cross-linked hydroxyethyl starch and an effective amount of a material selected from the class consisting of carboxyalkyl cellulose ethers, XC polymer and mixtures thereof.

In yet another embodiment of the present invention,
25 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 material selected from the class consisting of carboxyalkyl cellulose ethers, XC polymers and mixtures thereof.

30 One of the polymeric components (Polymer A) of the novel compositions of the present invention include a material selected from the class consisting of carboxyalkyl cellulose ethers wherein the alkyl group has from 1-3 carbon atoms such as carboxymethyl cellulose (CMC), carboxy-
35 ethyl cellulose (CEC), etc.; xanthan gum (xanthomonas polysaccharide gum biopolymer) known commonly as XC polymer; and mixtures thereof. The term polymeric component is

intended to include one or more of the carboxyalkyl cellulose ethers with or without XC polymer. Of the above named polymers, the preferred polymers are XC polymer and carboxymethyl cellulose.

5 The XC 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" XC polymer. The term "activated" as used herein refers to an
10 XC 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 XC polymers are to be found in published British Patent Application
15 No. 2075041 A. As disclosed in the aforementioned patent application, XC 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 XC polymer which will solubilize in a brine
20 having a density in excess of 1.701 g/ml at room temperature can be considered an "activated" XC polymer. It is to be understood, however, that the present invention is not limited to the use of such activated XC polymers. Depending upon the condition of mixing, and the composition of the
25 aqueous well servicing fluid, unactivated or dry powder XC polymers are compatible with the aqueous well servicing fluids used in the present invention. The term "compatible" as used herein, means that the XC polymer can be solvated or solubilized in a given aqueous solution with the use of
30 mixing techniques such as rolling at elevated temperatures. Thus, an incompatible system is one in which the XC polymer will not solubilize in the brine regardless of the mixing conditions used.

35 The other polymeric component (Polymer B) of the compositions of the present invention is a cross-linked HES. Such hydroxyethyl starches are produced by introduction of non-ionic hydroxyethyl side groups 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/m³) of approximately 325 and a DS of about 0.4.

The cross-linked HES 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 XC polymers. Methods of activating the cross-linked HES 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 HES. Indeed, it is a feature of the present invention that all of the polymeric components 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 pre-solvation of the XC polymers 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 cross-linked HES (Polymer B) and an effective amount of XC polymer, a carboxyalkyl cellulose ether (CACE) polymer or mixtures thereof (Polymer A). It has been found that when either XC polymer, a CACE polymer or a mixture thereof are added to aqueous well servicing fluids together with HES, depending upon the nature of the fluid, synergistic enhancement of viscosity and/or fluid

loss control 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 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 HES (Polymer B) to XC polymer, CACE polymer or mixtures thereof (Polymer A) of from 10 to 90 to 90 to 10, preferably from 33 to 67 to 75 to 25. The polymeric composition of the present invention can be either in the form of a dry mixture of the HES and either the XC polymer, CACE polymer or mixtures thereof, or if preferred, it can be in the form of solvated or activated forms of the polymers. Thus, for example, the HES and the XC polymer can be activated and those activated solutions mixed together 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 XC polymer, CACE polymers or mixtures thereof. The relative amounts of the HES and the other polymeric component (Polymer A) 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.

In general, however, the weight ratio of the HES to the other polymer component 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.

In general, the well servicing fluids will contain the polymer components in amounts of from 1.4 to 28.53 g/ml of hydroxyethyl starch (Polymer B) and from 0.7 to 14.3 g/ml of the other polymeric component (Polymer A).

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. 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 alkaline earth metal, a Group Ib metal, a Group IIB metal, as well as water soluble salts of ammonia and other cations. The polymeric compositions are particularly useful in the preparation of low fluid loss, heavy brines, i.e. aqueous solutions of soluble salts of multi-valent 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 about 1.318 g/ml, more especially, those having a density greater than 1.4 g/ml e.g. from 1.438 to 2.301 g/ml, especially those having a density greater than 1.797 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.

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 brines having low fluid loss characteristics and low rheological characteristics.

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 cross-linked hydroxyethyl starch employed, unless otherwise indicated, was BOHRAMYL CR marketed by Avebe (Veendam, Holland).

Example 1

To show the synergistic effect on viscosity and fluid loss achieved by mixing HES and XC polymer, 2.853 g/ml of XC polymer at either 0 or 17.118 g/ml levels of BOHRAMYL CR were added to an aqueous 10% by weight NaCl solution and mixed for 25 minutes on a Multimixer. Thereafter, the samples were rolled at 65.5°C, cooled to 23.3°C and stirred for 5 minutes and the API rheology and fluid loss determined. The data obtained and given in Table I below show that the BOHRAMYL CR when admixed with the XC polymer synergistically decreased the fluid loss in the aqueous sodium chloride solution and increased the viscosity.

TABLE I

Sample Mark	1	2	3	4	5	6	7	8	9	10	11
XC Polymer, g/l	2.85	0	2.85	0	2.85	0	2.85	0	2.85	0	2.85
BOHRAMYL CR, g/l	0	17.12	17.12	17.12	17.12	17.12	17.12	17.12	17.12	17.12	17.12
D.S.	-	0.30	0.30	0.40	0.40	0.22	0.22	0.62	0.62	0.80	0.80
Crosslinked	-	Yes	Yes	Yes	Yes	No	No	No	No	No	No
<u>After 25 Minutes Mixing on a Multimixer</u>											
Apparent Viscosity, cp	2.5	9.5	30	6.5	23	8	21	5	13.5	3	13.5
Plastic Viscosity, cp	2	8	20	6	16	7	14	4	8.5	2	7.5
Yield Point, kg/m ²	0.05	0.15	0.95	0.05	0.68	0.10	0.71	0.10	0.5	0.10	0.59
pH	7.6	8.6	7.9	8.5	-	8.8	8.2	8.8	8.0	8.3	7.7
API Filtrate*, ml	26	30	7.5	17.3	6.0	NC	219	NC	NC	NC	NC

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

Apparent Viscosity, cp	8	11	28	6.5	22.5	8.5	19	4.5	11	3.5	13
Plastic Viscosity, cp	4	10	16	6	12	8	13.5	4	3	3	7.5
Yield Point, kg/m ²	0.39	0.10	0.68	0.05	1.03	0.05	0.51	0.05	0.78	0.05	0.56
pH	7.1	8.4	7.7	8.3	7.5	8.6	7.7	8.2	7.6	7.8	7.2
API Filtrate*, ml	240	33	32	19.5	6.6	71.5	250	NC	NC	NC	NC

*NC = No Control

Example 2

The procedure of Example 1 was followed with the exception that carboxymethyl cellulose (CMC) was employed rather than XC polymer. The results, given in Table II, 5 clearly show that the combination of cross-linked hydroxyethyl starch and the CMC polymer gives synergistic results both as to fluid loss and viscosity.

TABLE II

Sample Mark	1	2	3	4	5	6	7	8	9	10	11
CMC, g/l	2.85	0	2.85	0	2.85	0	2.85	0	2.85	0	2.85
BOHRAMUL CR, g/l	0	17.12	17.12	17.12	17.12	17.12	17.12	17.12	17.12	17.12	17.12
D.S.	-	0.30	0.30	0.40	0.40	0.22	0.22	0.62	0.62	0.80	0.80
Crosslinked	-	Yes	Yes	Yes	Yes	No	No	No	No	No	No
After 25 Minutes Mixing on a Multimixer											
Apparent Viscosity, cp	9	9.5	41.3	6.5	31	8	24	5	13	3	12
Plastic Viscosity, cp	7	8	25.5	6	20	7	18	4	11	2	10
Yield Point, kg/m ²	0.195	0.146	1.538	0.049	1.074	0.098	0.561	0.098	0.220	0.098	0.220
pH	6.9	8.6	8.5	8.5	-	8.8	8.7	8.8	8.4	8.3	7.9
API Filtrate*, ml	68	30	17	17.3	7.0	NC	80	NC	100	NC	100
After Rolling @ 65.5°C, Cooling to 23.3°C, and Mixing 5 Minutes											
Apparent Viscosity, cp	8	11	35	6.5	28.5	8.5	19	4.5	11	3.5	11
Plastic Viscosity	7	10	26	6	20	8	15	4	10	3	9
Yield Point, kg/m ²	0.049	0.098	0.879	0.049	0.830	0.049	0.391	0.049	0.098	0.049	0.171
pH	7.2	8.4	8.2	8.3	8.3	8.6	8.4	8.2	8.0	7.8	7.7
API Filtrate*, ml	153	33	45	19.5	8.0	71.5	142	NC	151	NC	150

*NC = No Control

It should be noted with regard to the data shown in Tables I and II that the cross-linked HES gives significantly better results than non-cross-linked material.

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Example 3

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To test the effectiveness of the polymeric compositions of the present invention on weighted drilling fluids, various amounts of BOHRAMYL CR and XC polymer were added to a 1.438 g/ml sodium chloride solution weighted with BAROID (Registered Trade Mark, a baryte weighting material marked by NL Baroid, Houston, Texas). The BOHRAMYL CR was first added to the sodium chloride solution and mixed with a Multimixer for 10 minutes. This was followed by the addition of the XC polymer and the mixing continued for 10 minutes after which the BAROID was added and further mixing continued on the Multimixer for an additional 10 minutes. API rheology and fluid loss measurements were obtained on the thus prepared drilling fluid. The fluid was rolled for 16 hours at 65.5°C and the rheological and fluid loss properties tested. Thereafter, the samples were cooled and stirred for 5 minutes and the properties again determined. The data obtained and given in Table III below show that the XC polymer, when combined with the BOHRAMYL CR, synergistically decreases the fluid loss and increase the viscosity in weighted drilling fluids. It was also noted that there was essentially no settling out of weighting material.

T A B L E I I I

<u>Sample Mark</u>	<u>1</u>	<u>2</u>	<u>3</u>
<u>MATERIALS, g/l</u>			
BOHRAMYL CR,	17.12	17.12	
XC Polymer		0.71	0.71
BAROID	570.6	570.6	570.6
<u>PROPERTIES AFTER MULTIMIXING BOHRAMYL CR 10 MIN., ADDING XC POLYMER, MIXING 10 MIN., ADDING BAROID, MIXING 10 MIN.</u>			
Apparent Viscosity, cp	16.0	23.0	7.0
Elastic Viscosity, cp	15.0	19.0	7.0
Yield Point, kg/m ²	0.098	0.391	0.0
10 Sec. Gel. kg/m ²	0.244	0.244	0.0
10 Min. Gel. kg/m ²	0.683	0.342	0.293
H	8.2	8.1	8.1
Filtrate Loss, API, ml	11.5	8.8	57.4
<u>PROPERTIES AFTER ROLLING 16 HR. AT 65.5°C, TESTED HOT</u>			
Apparent Viscosity, cp	13.5	17.0	5.5
Elastic Viscosity, cp	13.0	14.0	5.0
Yield Point,	1.0	6.0	1.0
10 Sec. Gel.	8.0	3.0	1.0
10 Min. Gel.	14.0	11.0	15.0
<u>PROPERTIES AFTER COOLING AND STIRRING 5 MIN. MULTIMIXER</u>			
Apparent Viscosity, cp	17.5	24.5	6.5
Elastic Viscosity, cp	17.0	21.0	6.0
Yield Point, kg/m ²	0.049	0.342	0.049
10 Sec. Gel. kg/m ²	0.146	0.098	0.146
10 Min. Gel. kg/m ²	0.244	0.293	0.0
H	7.8	7.8	7.6
Filtrate Loss, API, ml	6.6	5.8	266
Settling of BAROID	med.	light	hvy.

Example 4

To test the effectiveness of the polymeric compositions of the present invention of viscosity enhancement and fluid loss control in heavy brines, e.g. brines containing calcium chloride, various amounts of HES and XC polymer were added to an aqueous, 5% calcium chloride solution and mixed for 20 minutes on a Multimixer and the API rheological properties determined (Initial Properties). Thereafter, the samples were rolled for 16 hours at 65.5°C, tested hot and unstirred. The samples were cooled, stirred 5 minutes on a Multimixer and the API rheology and fluid loss determined. The data obtained and given in Table IV below show that, when the BOHRAMYL CR and XC polymers are combined, they synergistically decrease the fluid loss in the aqueous calcium chloride solution and increase the viscosity.

TABLE IV

<u>Sample Mark</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
BOHRAMYL CR, g/l	25.68	17.12	15.41	14.26	0	0
XC Polymer, g/l	0	0	1.71	2.85	2.85	4.28

INITIAL PROPERTIES

Apparent Viscosity, cp	25.5	10	25.5	27.5	13	14.5
Plastic Viscosity, cp	19	8	21	15	12	10
Yield Point, kg/m ²	0.635	0.195	0.439	1.220	0.098	0.439
10 Sec. Gel., kg/m ²	0.049	0.098	0.244	0.342	0.098	0.195
10 Min. Gel., kg/m ²	0.049	0.098	0.244	0.439	0.195	0.293
pH	7.3	7.4	7.5	7.4	7.4	7.4

AFTER ROLLING 16 HR. AT 65.5°C TESTED HOT,
UNSTIRRED

Apparent Viscosity, cp	11	4.5	13	16.5	4.5	9
Plastic Viscosity, cp	8	4	8	7	3	4
Yield Point, kg/m ²	0.293	0.049	0.49	0.928	0.146	0.049
10 Sec. Gel., kg/m ²	0	0.049	0.098	0.195	0	s
10 Min. Gel., kg/m ²	0	0.049	0.146	0.244	0	0.098

AFTER COOLING AND MIXING 5 MIN. ON A MULTIMIXER

Apparent Viscosity, cp	29	11	21.5	26	7	12
Plastic Viscosity, cp	20	9	12	12	4	6
Yield Point, kg/m ²	0.879	0.195	0.928	1.367	0.293	0.586
10 Sec. Gel., kg/m ²	0.098	0.049	0.244	0.342	0	0.195
10 Min. Gel., kg/m ²	0.098	0.049	0.244	0.391	0	0.244
pH	7.4	7.4	6.8	6.7	5.6	5.6
API Filtrate, ml	6.7	9.0	7.3	7.1	226	194

Example 5

The procedure of Example 4 was followed except that following addition of the polymeric material to the calcium chloride solution, the equivalent of 71.3 g/l of Glen Rose shale was added and the compositions mixed for five minutes. Following this, the equivalent of 570.6 g/l of BAROID was added to the compositions and mixing on the Multimixer continued for an additional five minutes. The initial properties of the samples were then determined. The samples were rolled for 16 hours at 65.5°C and tested hot and unstirred. The samples were then cooled, mixed an additional five minutes on a Multimixer, and the API rheological and fluid loss properties determined. The data, given in Table V below, show that even in the presence of a weighting agent and a shale such as would be encountered in borehole drilling, there is synergistic enhancement of viscosity and control of fluid loss using a mixture of the BOHRAMYL CR and XC polymer. Additionally, solids settling is much lower in the case where a mixture of the polymers is utilized.

TABLE V

<u>Sample Mark</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
BOHRAMYL CR, g/l	25.68	17.12	15.41	14.26	0	0
XC Polymer, g/l	0	0	1.71	2.85	2.85	4.28
Glen Rose shale, g/l	71.32	71.32	71.32	71.32	71.32	71.32
BAROID, g/l	570.6	570.6	570.6	570.6	570.6	570.6

INITIAL PROPERTIES

Apparent Viscosity, cp	51	24	46.5	49.5	16	24
Plastic Viscosity, cp	31	20	33	18	12	15
Yield Point, kg/m ²	1.953	0.391	1.318	2.587	0.391	0.879
10 Sec. Gel., kg/m ²	0.976	0.342	0.490	0.732	0.146	0.293
10 Min. Gel., kg/m ²	1.318	0.586	0.732	0.928	0.244	0.342

AFTER ROLLING 16 HR. AT 65.5°C TESTED HOT,
UNSTIRRED

Apparent Viscosity, cp	35.5	15	36	35	13.5	21
Plastic Viscosity, cp	27	14	30	21	14	16
Yield Point, kg/m ²	0.830	0.098	0.586	1.367	0	0.537
10 Sec. Gel., kg/m ²	0.439	0.195	0.342	0.293	0.049	0.195
10 Min. Gel., kg/m ²	0.586	0.244	0.391	0.439	0.049	0.244

AFTER COOLING AND MIXING 5 MIN. ON A MULTIMIXER

Apparent Viscosity, cp	50.5	23.5	45.5	46	16	24
Plastic Viscosity, cp	34	18	33	26	14	16
Yield Point, kg/m ²	1.611	0.537	1.220	1.953	0.195	0.293
10 Sec. Gel., kg/m ²	0.490	0.293	0.490	0.586	0	0.195
10 Min. Gel., kg/m ²	1.025	0.586	0.683	0.781	0	0.244
pH	7.1	7.2	7.0	7.0	7.0	7.0
API Filtrate, ml	3.6	8.2	7.9	7.6	32.1	20.8
Settling of BAROID	Heavy Soft	Heavy Soft	Light ¹	None	Light ²	Light

¹trace to light; ²light to moderate.

Example 6

In this Example the effectiveness of the polymeric compositions of the present invention on weighted drilling fluids employing heavy brines, various amounts of BOHRAMYL CR and XC polymer were added to a 5% calcium chloride solution weighted with the equivalent of 570.6 g/l of BAROID was tested. The BOHRAMYL CR was first added to the calcium chloride solution and mixed with a Multimixer for 10 minutes. This was followed by the addition of the XC polymer and continued mixing for 10 minutes after which the BAROID was added and further mixing on the Multimixer continued for an additional 5 minutes. API rheology measurements (Initial Properties) were obtained on the thus prepared drilling fluid. The fluid was then rolled for 16 hours at 65.5°C and the rheological properties of the hot, unstirred drilling fluid obtained. Thereafter, the samples were cooled and stirred for 5 minutes and the rheological and fluid loss properties again determined. The data obtained and given in Table VI below shows the XC polymer, when combined with the BOHRAMYL CR, synergistically decrease the fluid loss and while increasing the viscosity in weighted drilling fluids. It should also be noted that when BOHRAMYL CR and XC polymer are combined, there is essentially no settling out of the BAROID weighting material.

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T A B L E VI

<u>Sample Mark</u>	<u>1</u>	<u>2</u>	<u>3</u>
BOHRAMYL CR, g/l	17.12	17.12	
XC Polymer, g/l		2.85	2.85
Glen Rose shale, g/l	71.32	71.32	71.32
BAROID, g/l	570.6	570.6	570.6
<u>INITIAL PROPERTIES</u>			
Apparent Viscosity, cp	24	56	16
Plastic Viscosity, cp	20	23	12
Yield Point, kg/m ²	0.391	2.880	0.391
10 Sec. Gel., kg/m ²	0.342	0.879	0.146
10 Min. Gel., kg/m ²	0.586	1.220	0.244
pH	7.1	7.2	7.1
<u>AFTER ROLLING 16 HR. AT 65.5°C</u> <u>TESTED HOT, UNSTIRRED</u>			
Apparent Viscosity, cp	15	46	13.5
Plastic Viscosity, cp	14	22	14
Yield Point, kg/m ²	0.098	2.295	0
10 Sec. Gel., kg/m ²	0.195	0.586	0.049
10 Min. Gel., kg/m ²	0.244	0.683	0.049
<u>AFTER COOLING AND MIXING 5 MIN.</u> <u>ON A MULTIMIXER</u>			
Apparent Viscosity, cp	23.5	60	16
Plastic Viscosity, cp	18	32	14
Yield Point, kg/m ²	0.537	2.734	0.195
10 Sec. Gel., kg/m ²	0.293	0.879	0
10 Min. Gel., kg/m ²	0.586	1.172	0
pH	7.2	7.0	7.0
API Filtrate, ml	8.2	5.0	32.1
Settling of Solids	Heavy Soft	None	Light to Moderate Soft

Example 7

The procedure of Example 4 was followed using differing amounts of BOHRAMYL CR and XC polymer. The data, given in Table VII below, clearly show the synergistic effect on viscosity and fluid loss control using a mixture of BOHRAMYL CR and XC polymers.

T A B L E VII

<u>Sample Mark</u>	<u>1</u>	<u>2</u>	<u>3</u>
BOHRAMYL CR, g/l	17.12	17.12	
XC Polymer, g/l		2.85	2.85
<u>INITIAL PROPERTIES</u>			
Apparent Viscosity, cp	10	30.5	13
Plastic Viscosity, cp	8	16	12
Yield Point, kg/m ²	0.195	1.416	0.098
10 Sec. Gel., kg/m ²	0.098	0.391	0.098
10 Min. Gel., kg/m ²	0.098	0.439	0.195
<u>AFTER ROLLING 16 HR. AT 65.5°C TESTED HOT, UNSTIRRED</u>			
Apparent Viscosity, cp	4.5	19	4.5
Plastic Viscosity, cp	4	10	3
Yield Point, kg/m ²	0.049	0.879	0.098
10 Sec. Gel., kg/m ²	0.049	0.098	0
10 Min. Gel., kg/m ²	0.049	0.146	0
<u>AFTER COOLING AND MIXING 5 MIN. ON A MULTIMIXER</u>			
Apparent Viscosity, cp	11	30.5	7
Plastic Viscosity, cp	9	15	4
Yield Point, kg/m ²	0.195	1.513	0.293
10 Sec. Gel., kg/m ²	0.049	0.342	0
10 Min. Gel., kg/m ²	0.049	0.391	0
pH	7.4	7.0	5.6
API Filtrate, ml	9.0	6.5	226

Example 8

The procedure of Example 6 was followed except differing amounts of XC polymer were employed and the equivalent of 570.6 g/l of BAROID was added to the samples after
5 addition of the polymers, the samples being mixed for five minutes on a Multimixer. The samples were then rolled for 16 hours at 65.5°C and the API rheology determined (Initial Properties). The samples were then cooled, mixed five
10 minutes on a Multimixer and the API rheological and fluid loss properties determined. The data, given in Table VIII below, again demonstrate the dramatic, synergistic effect achieved on viscosity and fluid loss control using a mixture of the polymers. As can also be seen from the data in Table VIII, no settling out of the weighting agent, BAROID, occurs
15 using a mixture of the polymers.

T A B L E V I I I

<u>Sample Mark</u>	<u>1</u>	<u>2</u>	<u>3</u>
BOHRAMYL CR, g/l	17.12	0	17.12
XC Polymer, g/l	0	1.43	1.43

INITIAL PROPERTIES

Apparent Viscosity, cp	17.5	11.5	36
Plastic Viscosity, cp	17	11	27
Yield Point, kg/m ²	0.049	0.049	0.879
10 Sec. Gel., kg/m ²	0.146	0	0.244
10 Min. Gel., kg/m ²	0.342	0	0.439

AFTER ROLLING 16 HR. AT 65.5°C TESTED HOT, UNSTIRRED

Apparent Viscosity, cp	13	8	25
Plastic Viscosity, cp	14	11	19
Yield Point, kg/m ²	0	0	0.586
10 Sec. Gel., kg/m ²	0.098	0	0.098
10 Min. Gel., kg/m ²	0.195	0	0.244

AFTER COOLING AND MIXING 5 MIN. ON A MULTIMIXER

Apparent Viscosity, cp	19.5	10	38
Plastic Viscosity, cp	16	13	26
Yield Point, kg/m ²	0.342	0	1.172
10 Sec. Gel., kg/m ²	0.195	0	0.244
10 Min. Gel., kg/m ²	0.293	0	0.342
pH	7.1	7.0	7.1
API Filtrate, ml	10.4	61.8	6.7
Settling of BAROID	Heavy Soft	Heavy Hard	None

It should be noted with regard to the data shown in Tables I and II that the cross-linked HES gives significantly better results than non-cross-linked material.



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 polymeric component selected from carboxyalkyl cellulose ethers wherein the alkyl group has from 1 to 3 carbon atoms, xanthan gum and mixtures thereof, the relative amounts of hydroxyethyl starch and polymeric component being such as to decrease synergistically the fluid loss of the aqueous fluid.
2. A method as claimed in claim 1 wherein the aqueous fluid comprises an aqueous solution of at least one water soluble salt of a multi-valent 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.
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 2.301 g/ml.
6. A method as claimed in any preceding claim wherein the weight ratio of hydroxyethyl starch to polymeric component is from 10 to 90 to 90 to 10.
7. A method as claimed in claim 6 wherein the weight ratio is from 33 to 67 to 75 to 25.
8. A method as claimed in any preceding claim wherein the hydroxyethyl starch is activated before being dispersed in the aqueous fluid.



9. A method as claimed in claim 8 wherein the polymeric component comprises carboxymethyl cellulose which is activated before being dispersed in the aqueous fluid.

10. A method as claimed in claim 8 wherein the polymeric component comprises xanthan gum.

11. A composition for increasing the viscosity and decreasing the fluid loss of aqueous well servicing fluids comprising a mixture of an effective cross-linked hydroxyethyl starch and an effective amount of a polymeric component selected from carboxyalkyl cellulose ethers wherein the alkyl group has from 1 to 3 carbon atoms, xanthan gum and mixtures thereof, the relative amounts of hydroxyethyl starch and polymeric components being such as to decrease synergistically the fluid loss from the aqueous fluid.

12. A composition of claim 11 wherein the weight ratio of hydroxyethyl starch to polymeric component is from 10 to 90 to 90 to 10.

13. A composition as claimed in claim 12 wherein the ratio is from 33 to 67 to 75 to 25.

14. A composition as claimed in any of claims 11 to 13 wherein the hydroxyethyl starch is activated.

15. A composition as claimed in claim 14 wherein the polymeric component comprises activated carboxymethyl cellulose.

16. A composition as claimed in any of claims 11 to 13 wherein said polymeric component comprises xanthan gum.

17. 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 polymeric component



selected from carboxyalkyl cellulose ethers wherein the alkyl group has from 1 to 3 carbon atoms, xanthan gum and mixtures thereof, the relative amounts of hydroxyethyl starch and polymeric component being such as to decrease synergistically the fluid loss of the aqueous medium.

18. A composition as claimed in claim 17 wherein the aqueous medium comprises a solution of at least one water soluble salt of a multi-valent metal ion.

19. A composition as claimed in claim 18 wherein the water soluble salt is calcium chloride, calcium bromide, zinc chloride, zinc bromide, or a mixture thereof.

20. A composition as claimed in any of claims 17 to 19 wherein the aqueous medium has a density greater than 1.4 g/ml.

21. A composition as claimed in claim 20 wherein the density of the aqueous medium is from 1.438 to 2.301 g/ml.

22. A composition as claimed in any of claims 17 to 21 wherein the hydroxyethyl starch is activated.

23. A composition as claimed in claim 22 wherein the polymeric component is activated carboxymethyl cellulose.

24. A composition as claimed in claim 22 wherein the polymeric component comprises xanthan gum.

25. A composition as claimed in any of claims 17 to 24 wherein the weight ratio of hydroxyethyl starch to polymeric component is from 10 to 90 to 90 to 10.

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

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



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28. A composition as claimed in claim 17 and substantially as hereinbefore described with reference to any of the Examples.
