



(12) UK Patent (19) GB (11) 2 086 923 B

(54) Title of invention
Dispersible hydrophilic polymer compositions

(51) INT CL³; C08L 1/323/00 3/08
5/00

(21) Application No
8125937

(22) Date of filing
25 Aug 1981

(30) Priority data

(31) **196367**

(32) **14 Oct 1980**

(33) **United States of America
(US)**

(43) Application published
19 May 1982

(45) Patent published
18 Jan 1984

(52) Domestic classification
**C3U 10C 10D 12B1A6C 12B2E
12B2J 2AX 2C7 2CX
C3W 100 121 122
C3V AX
E1F PA
U1S 1248 1374 1761 C3U C3W
C3VE1F**

(56) Documents cited
**GB 1366242
GB 1347212
GB 1077351**

(58) Field of search
**C3U
C3V**

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GB 2 086 923 B

DISPERSIBLE HYDROPHILIC POLYMER COMPOSITIONS

The present invention relates to compositions for use as thickening agents in aqueous systems and to aqueous well servicing fluids prepared therefrom.

5 Thickened 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, and
10 other aqueous fluids in which an increase in viscosity is desired. It is known to use hydrophilic polymeric materials as thickening agents for aqueous mediums used in such well servicing fluids. However, many hydrophilic polymers are not readily hydrated, solvated or dispersed in aqueous systems
15 without elevated temperatures and/or mixing under high shear for extended periods of time. For example, many such polymers are poorly hydrated, solvated or dispersed in aqueous solutions containing one or more multivalent cation water soluble salts, such as heavy brines which are commonly used in
20 well servicing fluids. In many cases, as 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
25 prepare them off the well site.

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 1.32 g/ml.

5 Another object of the present invention is to provide new, polymeric compositions which exhibit enhanced fluid loss control in heavy brine solutions.

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

10 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 thickened aqueous well servicing fluids under conditions of low shear mixing.

15 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 polymer composition for thick-
20 ening aqueous media which comprises:

(i) a water dispersible, particulate, organic polymer which increases the viscosity or decreases the fluid loss of an aqueous medium, and normally forms agglomerates upon addition to an aqueous medium,

25 (ii) a solvating agent comprising a water miscible, polar organic liquid which when uniformly mixed with the polymer in a weight ratio of polymer to solvating agent of 1:2 produces a mixture with substantially no free liquid solvating agent present after remaining quiescent for one
30 week at ambient temperature in a sealed container, and

(iii) a diluting agent comprising an organic liquid which is not a solvating agent. Preferably, there is also included a compatibilizing agent which has the capability of gelling the diluting agent.

35 In still a further embodiment of the present invention the polymeric compositions described above can be admixed with an aqueous medium such as, for example, a heavy brine to produce well servicing fluids, e.g. a workover fluid.

The polymeric compositions of the present invention utilize, as the hydrophilic polymer, any particulate, organic polymer which is water soluble or water dispersible and, which upon solubilization or dispersion in an aqueous medium, will increase the viscosity, and which normally form agglomerates or lumps upon addition to an aqueous system or slowly hydrate, solvate or disperse in an aqueous system. Preferably, the hydrophilic polymer is selected from the group consisting of cellulose derivatives, water dispersible starch derivatives, polysaccharide gums and mixtures thereof. Exemplary cellulose derivatives are the carboxyalkyl cellulose ethers such as carboxymethyl cellulose and carboxyethyl cellulose; hydroxyalkyl cellulose ethers such as hydroxyethyl cellulose and hydroxypropyl cellulose; and mixed cellulose ethers such as: carboxyalkyl hydroxyalkyl cellulose, e.g. carboxymethyl hydroxyethyl cellulose; alkylhydroxyalkyl cellulose, e.g. methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose; alkylcarboxyalkyl cellulose, e.g. ethylcarboxymethyl cellulose. See U. S. Patent No. 4,110,230.

Exemplary starch derivatives are the carboxyalkyl starch ethers such as carboxymethyl starch and carboxyethyl starch; hydroxyalkyl starch ethers, such as hydroxyethyl starch and hydroxypropyl starch; and mixed starch ethers such as: carboxyalkyl hydroxyalkyl starch, e.g. carboxymethyl hydroxyethyl starch; alkyl hydroxyalkyl starch, e.g. methyl hydroxyethyl starch; alkyl carboxyalkyl starch, e.g. ethyl carboxymethyl starch. Exemplary polysaccharide gums include: the bipolymers such as xanthomonas (xanthan) gum; galactomannan gums, such as guar gum, locust bean gum, tara gum; glucomannan gums; and derivatives thereof, particularly the hydroxyalkyl derivatives. For other exemplary polysaccharide gums see U. S. Patents Nos. 4,021,355 and 4,105,461. Especially preferred hydrophilic polymers are xanthan gum (XC polymer), carboxymethyl cellulose and hydroxyethyl starch.

Usually, upon the addition of dry, powdered hydrophilic

polymers to water, the polymer particles undergo hydration preventing the interior of the particle from readily hydrating, solvating or otherwise dispersing in the aqueous medium. Accordingly, high shear, long mixing times and/or elevated temperatures must be applied in order to obtain a homogeneous system. It is a feature of the present invention that the polymeric compositions of the present invention readily hydrate, dissolve or disperse in aqueous mediums at relatively low shear and ambient temperature. The thickening agents or polymeric compositions herein are liquids, pumpable and pourable.

In addition to the polymer, there is present in the compositions a solvating agent. Generally speaking, the solvating agent comprises a water miscible, polar organic liquid which exhibits a swelling effect on the polymer. Many compounds can be utilized as solvating agents depending upon the end use of the thickening agent. In determining whether a particular compound or material will function as a solvating agent according to the present invention, a simple test can be utilized as follows: one (1) part by weight of the hydrophilic polymer is uniformly mixed, as by spatulating, with two (2) parts by weight of the candidate solvating agent. The mixture is then allowed to set, in a quiescent state, for one week at ambient temperature in a container, preferably sealed. Liquids which are useful as solvating agents when subjected to the test procedure produce solid, semi-solid or viscous mixtures with no free liquid present in the mixture after the one week solvating period. Generally speaking, it has been found that virtually any organic compound which passes the solvation test described above will function, to a usable degree, as a solvating agent. Non-limiting but preferred solvating agents include: aliphatic glycols containing from 2 to 5 carbon atoms such as ethylene glycol, 1,2-propanediol, 1,4-butanediol, 1,3-pentanediol and the like; alkylene triols containing from 2 to 6 carbon atoms such as glycerol, 1,2,3-butane-triol, 1,2,3-pentanetriol, and the like; lower molecular weight polyalkylene glycols containing 4 to 9 atoms, such

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as diethylene glycol, triethylene glycol, and the like; amides containing from 1 to 4 carbon atoms such as formamide, acetamide, dimethyl formamide, and the like; and the mixtures of the various above compounds. Generally speaking, the solvating agent, depending on its ability to swell the polymer, will be present in the compositions, in a weight ratio of solvating agent to polymer of 1:1 to 5:1, preferably in the range from 2:1 to 4:1.

The diluting agent, in general, will be any liquid organic compound or material which is not a solvating agent. In general, the diluting agents are liquids which do not appreciably swell the polymers, i.e. they do not produce semi-solid or viscous mixtures which have no free liquid present after the one week solvation period described in the above test for determining solvating agents. Non-limiting examples of diluting agents include liquid aliphatic and aromatic hydrocarbons containing from 5 to 10 carbon atoms, kerosene, diesel oil, isopropanol, certain alkylene glycol ethers, vegetable oils, etc. Particularly preferred are organic liquids which are water soluble or miscible most preferably alkanols having at least 3 carbon atoms, ethylene glycol monoalkyl ethers, dialkylene glycol monoalkyl ethers, and the like. The diluting agent will preferably be present in an amount which will maintain the polymeric composition in a liquid, pourable state at a temperature of about 20°C. It will be understood, however, that lesser amounts of diluting agent can be used if desired and that the ultimate amount of diluting agent employed will depend upon the type of shear which is available to disperse the thickener. In general, it has been found that desirable thickeners, which are pourable liquids, can be produced from compositions containing from 10 to 25% by weight hydrophilic polymer, from 2 to 70% by weight diluting agent, and from 5 to 88% solvating agent.

It is preferable that a compatibilizing agent also be used. The compatibilizing agent will be a material which will disperse in the diluting agent, increase the viscosity of the

diluting agent, reduce syneresis and, in general, aid in providing a homogeneous combination of the polymer, the solvating agent and the diluting agent.

Non-limiting examples of compatibilizing agents
5 include organophilic hectorites, organophilic attapulgites, organophilic bentonites and the like. Such organophilic clays are produced by methods and have a composition described in U.S. Patents Nos. 2,966,506 and 4,105,578.

10 In addition, the compatibilizing agent can include finely divided siliceous materials such as fumed silica, surface treated silicas such as silane treated silicas, etc. Particularly preferred compatibilizing agents are the organophilic clays
15 described in U.S. Patent No. 4,105,578.

Such clays are formed by the reaction of a methylbenzyl dialkyl ammonium compound, wherein the ammonium compound contains 20 to 25% alkyl groups having 16 carbon atoms and 60 to 75% alkyl groups
20 having 18 carbon atoms, (based on number of alkyl groups), and a smectite-clay having a cationic exchange capacity of at least 75 milliequivalents per hundred grams of said clay, and wherein the amount of said ammonium compound is from 100 to 120 milliequivalents
25 per hundred grams of said 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
30 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
35 tallow ammonium bentonite.

When an organophilic clay is used as the compatibilizing agent, it is preferable to use a

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dispersant to enhance the dispersability of the organophilic clay in the diluting agent. Generally speaking, the dispersant is a low molecular weight, polar organic compound such as a lower molecular weight alcohol, a lower ketone, a lower alkylene carbonate and the

like. 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 methanol and from 25 to 2% by weight water. Advantageously, the dispersant may comprise one of the solvating agents mentioned above. Thus, for example, a part of the solvating agent can be used to disperse the compatibilizing agent into the diluting agent. It will be understood that the dispersant, while desirable, is optional since its function is to aid in forming a homogeneous suspension of the organophilic clay, i.e. the compatibilizing agent, in the diluting agent. Such a homogeneous suspension can be achieved by mixing techniques well known in the art. When employed, the dispersant will be present in an amount of from 1.5 to 80% by weight, based on the weight of the compatibilizing agent, preferably from 20 to 40% by weight, based on the weight of the compatibilizing agent.

The compatibilizing agent need only be present in the composition in an amount sufficient to keep the blend of the polymer, the solvating agent and all or a part of the diluting agent from solidifying. Preferably, the compatibilizing agent will be present in an amount, based on the amount of diluting agent plus compatibilizing agent, of from 2.85 to 71.5 g/l, most preferably from 14.25 to 43 g/l.

While the polymeric compositions of the present invention are useful as thickeners or suspending agents in suspension fertilizers, liquid pesticides, liquid herbicides, and other aqueous systems which require viscosity enhancement, they are particularly useful in the preparation of well servicing fluids and, more particularly, well servicing fluids made from aqueous mediums containing soluble salts such as, for example, a soluble salt of an alkali metal, an alkaline

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earth metal, a Group Ib metal, a Group IIb metal, as well as water soluble salts of ammonia and other cations. The thickener compositions are particularly useful in the preparation of thickened heavy brines, i.e. aqueous solutions of soluble salts of multivalent cations, e.g. Zn and Ca.

The most preferred thickened heavy brines, particularly those used for well servicing fluids, are made from brines having a density greater than 1.32 g/ml.

Especially preferred heavy brines comprise water solutions of salts selected from the group consisting of calcium chloride, calcium bromide, zinc chloride, zinc bromide, and mixtures thereof.

The use of a solid, particulate inert filler in the compositions of the present invention aids in dispersibility and increases the rate of hydration of the polymer compositions in heavy brine solutions. Accordingly, the desired rheology is obtained at a faster rate when the polymer solutions are added to such brines. The filler should be a material which exhibits little or no absorption capacity for the solvating agent and is, in general, non-reactive with the hydrophilic polymer, solvating agent or the diluting agent. Non-limiting examples of such solid, particulate, inert fillers include kaolin, alumina, silica, diatomaceous earth, oil soluble resins, alkaline earth metal carbonates, alkali metal carbonates, etc. When employed, the inert filler will be present in a weight ratio of polymer to filler of from 1:1 to 1:10.

It has been found that if the polymer compositions or thickeners are aged before being added to heavy brines, the hydration rate in such brines is increased. Accordingly, although the polymer compositions or thickeners may be added to the heavy brines within several hours of their preparation, longer aging times increase the rate at which the thickeners hydrate in the heavy brines.

To more fully illustrate the present invention, the following non-limiting examples are presented. Unless other-

wise indicated, all physical property measurements were made in accordance with testing procedures set forth in STANDARD PROCEDURE FOR TESTING DRILLING FLUID API RP 13B, Seventh Edition, April, 1978. The physical property parameters referred to in the examples, unless otherwise indicated, are in units expressed as follows:

- 300 rpm = Fann V-G Meter dial reading at 300 rpm
- PV = API Plastic Viscosity (cps)
- YP = API Yield Point (Kg/m²)
- 10 GELS = 10-sec gel/10 min. gel where 10-sec gel
= API 10-sec gel strength (Kg/m²)
10-min. gel = API 10-min. gel strength (Kg/m²)

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EXAMPLE 1

Polymer 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 Dispensator for 20 minutes, 8,000 parts by weight diesel oil, 160 parts by weight GELTONE II (Tradename of an organophilic bentonite marketed by NL Baroid, Houston, Texas) and 45.5 parts by weight of a 95/5 (weight ratio) mixture of methanol and water, the latter mixture functioning as a dispersion aid for the organophilic clay;

(2) To 200 gm. of this stock diesel mixture were added 100 gm. of XC polymer while mixing with a Multimixer, and the mixing was continued for 2 minutes;

(3) 100 gm. of a potential solvating agent were added and the mixing was continued for 5 minutes;

(4) Thereafter the polymer compositions were allowed to set for at least 16 hours before being evaluated. The polymer compositions were evaluated in a 2.30 g/ml brine solution containing calcium bromide and zinc bromide at a thickener concentration of 34.24 g/l (8.56 g/l XC polymer) by the following procedure:

(1) 350 ml of the brine and 4 gm. of the polymer composition (thickener) were mixed together for 5 minutes with a Multimixer;

(2) The rheological properties were measured;

(3) The samples were placed in pint (500 ml) jars in a roller oven at a temperature of 65.5°C and rolled overnight;

(4) The rheological properties were obtained after the samples had cooled to room temperature. The data obtained are given in Table I below.

For comparison purposes, polymeric compositions were prepared in which the stock diesel mixture was substituted for the solvating agent (designated NONE). Also

the dry powdered unsolvated XC polymer was evaluated in the $\text{CaBr}_2/\text{ZnBr}_2$ brine. As can be seen from the data in Table 1, numerous compounds

function as solvating agents. Additionally, it can be seen that without a solvating agent the hydration rate is greatly reduced as evidenced by poor rheological properties.

Table 1

8.56 g/l XC Polymer in 2.30 g/ml $\text{CaBr}_2/\text{ZnBr}_2$ Solution

<u>Solvating Agent</u>	<u>Initial Rheology*</u>				<u>Final Rheology**</u>			
	300	PV	YP	GELS	300	PV	YP	GELS
None	23	17	0.29	1/3	104	51	2.59	3/3
Ethylene Glycol	35	32	0.15	1/1	103	69	1.66	2/2
Diethylene Glycol	43	38	0.24	1/1	169	94	0.37	6/6
Triethylene Glycol	27	27	0	1/1	151	89	3.03	4/4
1, 3-Propane diol	26	18	0.39	1/1	148	58	4.39	5/5
Glycerin	28	28	0	1/1	157	92	3.17	3/4
None-Dry Powder XC Polymer	20	13	0.34	1/-	76	48	1.37	2/2

* After 5 minutes on a Multimixer

** After rolling overnight @ 65.5°C

Example 2

Polymer compositions were prepared using the following procedure:

- (1) 200 gm. of diesel oil, 7 gm. of GELTONE[®] II organophilic clay, and 2.4 ml. of the 95/5 mixture of methanol and water were mixed on a Multimixer for 15 minutes;
- (2) 100 gm. of the polymer indicated in Table 2 were added and mixed 2 minutes;
- (3) 100 gm. of the solvation aids indicated in Table 2 were added and mixed 2 minutes;
- (4) Thereafter the polymer compositions were allowed to set for one hour before being evaluated.

The polymer compositions were evaluated at a concentration of 22.82 g/l (5.70 g/l polymer) in the 2.3 g/ml CaBr₂/ZnBr₂ brine. The API rheology was obtained after mixing 15 minutes on a Multimixer and after the samples were rolled for 16 hours at 65.5°C. The data obtained are given in Table 2.

Table 2

<u>Polymer</u>	<u>Solvation Aid*</u>	<u>Initial Rheology</u>			<u>Final Rheology</u>		
		<u>PV</u>	<u>YP</u>	<u>10 Sec. Gel</u>	<u>PV</u>	<u>YP</u>	<u>10 Sec. Gel</u>
CELLEX ¹ CMC	70% EG, 30% NVP	20	0.10	0.10	32	0	0.10
CELLEX CMC	EG	20	0.05	0.10	25	0.15	0.10
XC Polymer	70% EG, 30% NVP	23	0.10	0.10	59	2.10	0.24
XC Polymer	EG	22	0.15	0.10	57	1.81	0.20

¹ Tradename of a sodium carboxymethyl cellulose (CMC) marketed by NL Baroid, Houston, Texas

* EG = Ethylene Glycol; NVP = N-Vinyl Pyrrolidone; % by weight

Example 3

Polymer compositions were prepared using the procedure of Example 1. The polymer compositions were evaluated in an 1.39 g/ml calcium chloride brine solution at the concentrations listed in Table 3. The samples were prepared as in Example 1. After the rheological properties were obtained on the samples rolled at 65.5°C, 28.53 g/lof BARACARB (Tradename of a calcium carbonate bridging agent marketed by NL Baroid, Houston, Texas) were added and mixed 2 minutes on a Multimixer. The API RB13B low temperature filtration test was then conducted on each sample. For comparison, the dry powder polymers were evaluated at the same concentration. The data obtained are given in Table 3.

Table 3

Polymer	Polymer Comp. (g/l)	Polymer (g/l)	Initial Rheology			Final Rheology			API Fluid Loss ml.
			300	PV	YP	300	PV	YP	
CELLEX (Carboxymethyl Cellulose) ¹	57.05	14.26	*	*	*	*	*	*	18.6
	--	14.26	*	*	*	*	*	*	34
XC Polymer (Xanthomonas Biopolymer)	34.24	8.56	20	14	0.29	1/-	74	29	1.6
	--	8.56	8	8	0	1/1	69	24	2.2
LOLOSS ¹ (Guar Gum)	34.24	8.56	171	57	5.57	21/1	190	54	2.9
	--	8.56	133	63	3.42	14/-	191	53	23.5
Hydroxypropyl Starch	57.05	14.26	21	19	0.10	0/-	18	16	5.4
Hydroxypropyl Starch	--	14.26	10	10	0	0/-	14	12	86
DEXTRID ² (Modified Starch)	57.05	14.26	38	22	0.78	1/-	19	16	60
	--	14.26	*	*	*	*	*	*	28.4

* No dispersion of polymer

¹ Tradename of a guar gum marketed by NL Baroid/NL Industries, Inc.

² Tradename of a modified starch marketed by NL Baroid/NL Industries, Inc.

Example 4

The following example demonstrates the solvation of XC polymer and BOHRAMYL CR (Tradename of a non-ionic hydroxyethyl starch marketed by Avebe, Veendam, Holland) and their use as fluid loss control additives in heavy brines.

Sample A

An XC polymer composition was prepared by mixing together 20% by weight XC polymer, 25% glycerol, 54.6% isopropanol, and 0.4% CAB-O-SIL M5 (fumed silica) and aging 16 hours.

Sample B

The BOHRAMYL CR composition was prepared by mixing together 20% by weight BOHRAMYL CR, 25% glycerol, 54.6% isopropanol, and 0.4% CAB-O-SIL M5 and aging for 16 hours.

Samples A and B were evaluated at a concentration of 15 ppb (3 ppb XC polymer or BOHRAMYL CR) in a 1.92 g/ml $\text{CaBr}_2/\text{ZnBr}_2$ solution. The solutions were stirred with a Fann V-G meter at 300 rpm for 1 hour and the dial reading was obtained initially and after 30 and 60 minutes. The solutions were rolled overnight at 65.5°C , cooled to room temperature and again evaluated. Thereafter 28.53 g/l of BARACARB were added to each solution and the API filtration test conducted on each. As can be seen from the data obtained and given in Table 4, both the XC polymer and the BOHRAMYL CR act as good filtrate control agents in the presence of a calcium carbonate bridging agent after hot rolling.

Table 4

8.56 g/l Additive in 1.92 g/ml Solution

<u>Sample</u>	<u>300 rpm Fann V-G Dial Reading</u>				<u>API Filtrate ml.</u>
	<u>Minutes at 300 rpm</u>			<u>After Rolling</u>	
	<u>0</u>	<u>30</u>	<u>60</u>		
A	19	24	26	91	28
B	12	13	15	23	10.8

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In the following examples, brine systems in which the polymeric suspensions were tested were as follows:

1.39 g/ml	CaCl ₂
1.70 g/ml	CaBr ₂
1.80 g/ml	CaCl ₂ /CaBr ₂
1.82 g/ml	CaCl ₂ /CaBr ₂ /ZnBr ₂
1.86 g/ml	CaBr ₂ /ZnBr ₂
1.92 g/ml	CaBr ₂ /ZnBr ₂
2.30 g/ml	CaBr ₂ /ZnBr ₂

Example 5

Sample A

Suspensions of XC polymers were made in the following manner: 58.8% of isopropanol and 0.2% by weight of CAB-O-SIL^(registered trademark) were mixed on a Multimixer for 2 minutes. Following this, 20% by weight of the XC polymer was added and the mixing carried out for an additional minute. Twenty-two percent by weight of glycerol was then added and the mixing continued an additional 1 minute.

After standing overnight, the suspensions were tested at a concentration of 3.56 g/l XC polymer in brines of various densities. Rheology was taken on the Fann Model 35-A after rolling 1 hour at room temperature and again after rolling overnight at 55.5°C. The API filtrate was run after adding 28.53 g/l calcium carbonate bridging agent to each sample.

Sample B

The method used in preparing Sample A of Example 5 was carried out except the suspension contained 40% by weight isopropanol, 20% by weight XC polymer and 40% by weight glycerol.

Control samples in which dry powder was added directly to each brine at the 8.56 g/l level were also tested in the same manner. The results are given in Table 5.

Table 5

8.56 g/l XC Polymer in Brine Solution

Solvating Agent	Brine Solution (g/ml)	API Rheology					API Fluid*	
		One Hr. @ R.T.		16 Hrs. @ 65.5°C			Loss (ml)	
		600	300	3	600	300		
NONE	1.39	17	9	0.5	147	98	23	9.2
22% Glycerol	1.39	22.5	12	1	OS**	125	17	4.0
40% Glycerol	1.39	19	10	1	OS	OS	--	16.0
NONE	1.70	15	8	1	29	15	2	3.3
22% Glycerol	1.70	24.5	12.5	1	72	45	25	0.5
40% Glycerol	1.70	32.5	16	1	100	59	3	1.0
NONE	1.80	85	43	2	162	87.5	2	5.1
22% Glycerol	1.80	90	46.5	1	OS	224	12	0
40% Glycerol	1.80	119	61	2	OS	OS	--	0
NONE	1.82	70	36	2	123	65	2	8.9
22% Glycerol	1.82	76	39	0.5	OS	216	10	0
40% Glycerol	1.82	136	71	2	200	135	6	2.0
NONE	1.86	24	13	2	145	107	22	5.8
22% Glycerol	1.86	59	33.5	2	99	65	3	3.9
40% Glycerol	1.86	150	100	20	174	126	27	3.0

*28.53 g/l BARACARB CaCO₃ bridging agent added to hot rolled brine

** Off Scale

Table 5 (cont'd)

8.55 g/l XC Polymer in Brine Solution

Solvating Agent	Brine Solution (g/ml)	API Rheology					API Fluid* Loss (ml)	
		One Hr. @ R.T.		16 Hrs. @ 65.5°C				
		600	300	3	600	300		3
NONE	1.92	24	12	0	127	85	15	17
22% Glycerol	1.92	58	30	1	136	93	7	3.8
40% Glycerol	1.92	145	100	17	177	125	31	5.0
NONE	2.30	43	22	0.5	246	168	16	33
22% Glycerol	2.30	84	45	2	231	152	9	19.4
40% Glycerol	2.30	230	157	15	277	188	20	40

*28.53 g/l BARACARB CaCO₃ bridging agent added to hot rolled brine

As can be seen from the data in Table 5, activation of the XC polymer with the glycerol produced enhanced viscosities. Additionally, API fluid loss control was enhanced in the activated or solvated polymer as opposed to the unactivated polymer.

Example 6

The procedure of Example 5, Sample A, was followed using DEXTRID (Tradename of a bacterially stabilized pre-gelatinized starch marketed by NL Baroid). The results are given in Table 6.

Table 6

8.56 g/l DEXTRID Polymer in Brine Solution

Solvating Agent	Brine Solution (g/ml)	API Rheology						API Fluid* Loss (ml)
		One Hr. @ 23°C		16 Hrs. @ 65.5°C				
		600	300	3	600	300	3	
NONE	1.39	18	9	1	27	14	0.5	130
Glycerol	1.39	17	8.5	0.5	24	12	1	136
NONE	1.70	14	8	0.5	69	42	5	5.4
Glycerol	1.70	16	7	1	28	14	0.5	2.2
NONE	1.80	85	43	0.5	190	105	3	43
Glycerol	1.80	82	41	1	146	76	1	23
NONE	1.82	68	34	2	120	68	2	44
Glycerol	1.82	72	36	0.5	119	66	2.5	15
NONE	1.86	15	9	0.5	48	24	1	24
Glycerol	1.86	20	10	0.5	53	25	1	7.6
NONE	1.92	20	10	0.5	56	27	2	27
Glycerol	1.92	20	10	0.5	42	20	1	10
NONE	2.30	39	19	0.5	90	47.5	2	26
Glycerol	2.30	51	25	1	107	49	2	1.8

*28.53 g/l BARACARB CaCO₃ bridging agent added to hot rolled brine

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Example 7

The procedure of Example 5, Sample A, was followed using as a polymer IMPERMEX (Tradename of a pre-gelatinized starch marketed by NL Baroid). The results are given in Table 7.

Table 7

8.56 g/l IMPERMEX Polymer in Brine Solution

Solvating Agent	Brine Solution (g/ml)	API Rheology						API Fluid * Loss (ml)
		One Hr. @ 23°C		16 Hrs. @ 65.5°C				
		600	300	3	600	300	3	
NONE	1.39	D30	16	1	D23	12	1	322
Glycerol	1.39	29.5	16	1	27.5	14.5	2	327
NONE	1.70	17	9	1	55	32	5	4.8
Glycerol	1.70	21	11	2	29	16	0.5	4.8
NONE	1.80	87	44	1	155	84	3	108
Glycerol	1.80	100	52.5	1	151	81	3	75
NONE	1.82	70	36	2	118	63	3	NC**
Glycerol	1.82	85	44	2	132.5	71	2	63
NONE	1.86	21	11	2	32	17	0.5	154
Glycerol	1.86	27	14	0.5	31	16	0.5	75
NONE	1.92	20	10	0.5	35	19	0.5	9.8
Glycerol	1.92	38	14	2	37	20	1	6.6
NONE	2.30	42	21	0.5	79	42	2	NC
Glycerol	2.30	59	30	1	84	45	3	2.2

*28.53 g/l BARACARB CaCO₃ bridging agent added to hot rolled brine

** NC = No Control

Example 8

The procedure of Example 5, Sample A, was followed using CELLEX (Tradename of a sodium carboxymethyl cellulose (CMC) marketed by NL Baroid, Houston, Texas). The results are given in Table 8.

Table 8

8.56 g/l CELLEX Polymer in Brine Solution

Solvating Agent	Brine Solution (g/ml)	API Rheology						API Fluid* Loss (ml)
		One Hr. @ 23°C		16 Hrs. @ 65.5°C				
		600	300	3	600	300	3	
NONE	1.39	116	08	1	17	10	0.5	220
Glycerol	1.39	15	8	0.5	22	11	0.5	26.2
NONE	1.70	14	7	5	15	17	0.5	288
Glycerol	1.70	13.5	7	1	14	8	6	158
NONE	1.80	84	43	1	95	48	2	218
Glycerol	1.80	76.5	39	0.5	95	49	0.5	208
NONE	1.82	69	35	2	75	38	2	NC**
Glycerol	1.82	70	35	2	84	43	0.5	314
NONE	1.86	15	8	4	16	9	0.5	304
Glycerol	1.86	17	9	0.5	17.5	9	1	343
NONE	1.92	17	10	2	18	9	7	290
Glycerol	1.92	18	10	1	19	10	0.5	318
NONE	2.30	100	19	2	44	24	2	NC
Glycerol	2.30	42	21	1	90	49	2	35

*28.53 g/l BARACARB CaCO₃ bridging agent added to hot rolled brine

** NC = No Control

Example 9

(Registered Trademark)

The procedure of Example 5 was followed using DRISPAC_L (Tradename of a polyanionic carboxymethyl cellulose marketed by NL Baroid). The results are given in Table 9.

Table 9

8.56 g/l DRISPAC Polymer in Brine Solution

Solvating Agent	Brine Solution (g/ml)	API Rheology						API Fluid * Loss (ml)
		One Hr. @ 23°C		16 Hrs. @ 65.5°C				
		600	300	3	600	300	3	
NONE	1.39	16	9	1	21	111	2	44
Glycerol	1.39	17	9	1	33	17	1	5.5
NONE	1.70	15	8	1	15	8	0.5	296
Glycerol	1.70	14.5	8	1	16	9	0.5	288
NONE	1.80	85	43	2	101	52	2	126
Glycerol	1.80	83	42.5	1	214	118	3	1.1
NONE	1.82	70	36	2	75	38	2	NC**
Glycerol	1.82	74	38	2	91	46	3	212
NONE	1.86	16	8	0.5	17	9	0.5	298
Glycerol	1.86	18	9	2	16	8	0.5	336
NONE	1.92	17	9	0	17	9	0.5	280
Glycerol	1.92	20	10	0.5	20	10	0.5	312
NONE	2.30	39	20	0.5	50	26	2	NC
Glycerol	2.30	45	23	2	258	166	110	0.4

*28.53 g/l BARACARB CaCO₃ bridging agent added to hot rolled brine

** NC = No Charge

Example 10

Polymeric suspensions of BOHRAMYL CR cross-linked hydroxyethyl starch were made according to the following method:

- 5 1. 57.8% by weight of a diluting agent comprised of either isopropanol (IPA) or ethylene glycol monobutylether (Butyl Cellosolve[®]) were admixed on a Multimixer for 1 minute with 0.2 weight percent of CAB-O-SIL. Twenty percent by weight of BOHRAMYL CR was then added and the mixing continued for an
10 additional minute. Glycerol, in an amount of 22% by weight, was then added and an additional 1 minute of mixing carried out. The samples were allowed to stand overnight after which they were tested at 8.56 g/l active polymer basis in brines of various densities. Rheology data was obtained on a Fann Model
15 35-A after rolling 1 hour at room temperature and again after rolling overnight at 65.5°C. API filtrates were run after the addition of 28.53 g/l CaCO_3 bridging agents. Control samples in which 8.56 g/l CaCO_3 dry powdered BOHRAMYL CR was added to each brine were tested in the same manner. The data are given in Table
20 10.

Table 10

8.56 g/l BOHRAMYL in Brine Solutions

Solvating Agent	Diluting Agent	Brine Solution (g/ml)	One Hr. @ R.T.			API Rheology			16 Hrs. @ 65.5°C			API Fluid* Loss (ml)
			600	300		3	600	300	3			
NONE	NONE	1.39	032	17	2	36	19	1	30			
Glycerol	IPA	1.39	37	19	1	47	24	0.5	10.2			
Glycerol	Cellosolve	1.39	37	19	1	49	26	2	4.9			
NONE	NONE	1.70	30	16	0.5	38	19	1	10.4			
Glycerol	IPA	1.70	38	20	1	40	21	0.5	10.0			
Glycerol	Cellosolve	1.70	40	22	2	45	24	2	4.6			
NONE	NONE	1.80	66	33	9	195	105	3	0.8			
Glycerol	IPA	1.80	129	65	1	205	111	3	0.4			
Glycerol	Cellosolve	1.80	141	75	2	281	151	4	0.2			
NONE	NONE	1.82	87	52	**	153	80	2	4.2			
Glycerol	IPA	1.82	90	45	1	163	84	2	4.6			
Glycerol	Cellosolve	1.82	116	60	2	188	97	3	1.0			
NONE	NONE	1.86	19	10	0.5	35	18	1	10.3			
Glycerol	IPA	1.86	29	15	1	36	18	2	17.5			
Glycerol	Cellosolve	1.86	35	19	2	45	24	2	7.8			

*28.53 g/l BARACARB CaCO₃ bridging agent added to hot rolled brine

** lumps

Table 10 (cont'd)
8.56 g/l BOHRAMYL in Brine Solutions

Solvating Agent	Diluting Agent	Brine Solution (g/ml)	API Rheology				API Fluid * Loss (ml)	
			One Hr. @ R.T.		16 Hrs. @ 65.5°C			
			600	300	3	600	300	3
NONE	NONE	1.92	21	11	0.5	21	0.5	10.0
Glycerol	IPA	1.92	34	18	1	21	1	15.3
Glycerol	Cellosolve	1.92	37	19	2	24	2	9.6
NONE	NONE	2.30	37	19	2	115	63	0.1
Glycerol	IPA	2.30	69	34	1	98	52	0.2
Glycerol	Cellosolve	2.30	75	41	2	129	70	0.4

Example 11

5 A polymer suspension was prepared by mixing 100 grams of carboxymethyl starch (CMS), 200 grams of ethylene glycol, 50 grams of isopropanol and 5 grams of CAB-O-SIL M5 for 3 minutes on a Multimixer.

10 A second polymer suspension was prepared by mixing 10 parts by weight of XC polymer, 3 parts by weight of ethylene glycol, and 10 parts by weight of isopropanol containing 1% by weight KLUCEL H ^{Registered Trade Mark} (Tradename) of a hydroxypropyl cellulose marketed by Hercules, Inc. The XC and CMS polymer suspensions were mixed with a 1.92 g/ml $\text{CaBr}_2/\text{ZnBr}_2$ solution for 10 minutes on a Multimixer. The concentration of the XC and CMS polymers in the brine solution were ^{11.41 g/l} and 20.26 g/l respectively. The sample was divided into two equal portions and ^{14.26 g/l} of CaCO_3 were added to one sample. The samples were allowed to hydrate overnight at room temperature, and the API properties determined after rolling overnight at 65.5°C. The data obtained are given in Table 11.

Table 11

	<u>Sample</u>	
	<u>1</u>	<u>2</u>
XC Polymer, (g/l)	2.85	2.85
Carboxymethyl Starch, (g/l)	5.71	5.71
Calcium Carbonate, (g/l)	0	14.26
<u>Initial Properties After 15 Minutes on a Multimixer</u>		
Apparent Viscosity	14	15
Plastic Viscosity	12.5	13.5
Yield Point (Kg/m ²)	0.17	0.15
10 Sec. Gel Strength (Kg/m ²)	0.02	0.02
<u>Properties After Hydrating Overnight at 23°C</u>		
Apparent Viscosity	26	28
Plastic Viscosity	19	21
Yield Point (Kg/m ²)	0.71	0.71
10 Sec. Gel Strength (Kg/m ²)	0.05	0.05
API Filtrate	14	3.6
<u>Properties After Rolling Overnight at 65.5°C</u>		
Apparent Viscosity	26	23
Plastic Viscosity	19.5	21
Yield Point (Kg/m ²)	0.68	0.71
10 Sec. Gel Strength (Kg/m ²)	0.05	0.05
API Filtrate	35	17

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CLAIMS:

1. A polymer composition for thickening aqueous media which comprises:

(i) a water dispersible, particulate, organic polymer which increases the viscosity or decreases the fluid loss of an aqueous medium, and normally forms agglomerates upon addition to an aqueous medium,

(ii) a solvating agent comprising a water miscible, polar organic liquid which when uniformly mixed with the polymer in a weight ratio of polymer to solvating agent of 1:2 produces a mixture with substantially no free liquid solvating agent present after remaining quiescent for one week at ambient temperature in a sealed container, and

(iii) a diluting agent comprising an organic liquid which is not a solvating agent.

2. A composition as claimed in Claim 1 wherein the solvating agent is an aliphatic glycol containing from 2 to 5 carbon atoms, an alkylene triol containing from 3 to 5 carbon atoms, a polyalkylene glycol containing 4 to 9 carbon atoms, an amide containing from 1 to 4 carbon atoms, or a mixture thereof.

3. A composition as claimed in Claim 1 wherein the solvating agent comprises ethylene glycol or glycerine.

4. A composition as claimed in any preceding Claim wherein the diluting agent is a liquid aliphatic or aromatic hydrocarbon containing from 5 to 10 carbon atoms, diesel oil, kerosene, an alkanol containing at least 3 carbon atoms, or a mixture thereof.

5. A composition as claimed in any preceding Claim which comprises a compatibilizing agent capable of increasing the viscosity of the diluting agent.



6. A composition as claimed in Claim 5 wherein the compatibilizing agent comprises the reaction product of a methyl benzyl dialkyl ammonium compound, wherein the ammonium compound contains 20 to 35% alkyl groups having 16 carbon atoms and 60 to 75% alkyl groups having 18 carbon atoms, (based on a number of alkyl groups) and a smectite-type clay having a cationic exchange capacity of at least 75 milliequivalents per hundred grams of clay, the amount of ammonium compound being from 100 to 120 milliequivalents per 100 grams of clay, 100% active clay basis.

7. A composition as claimed in Claim 6 wherein the smectite-type clay is hectorite or sodium bentonite.

8. A composition as claimed in Claim 6 or 7 wherein the methyl benzyl dialkyl ammonium compound is methyl benzyl dihydrogenated tallow ammonium chloride.

9. A composition as claimed in Claim 5 wherein the compatibilizing agent is a particulate silica gelling agent.

10. A composition as claimed in any preceding Claim wherein the weight ratio of solvating agent to polymer is from 1:1 to 5:1.

11. A composition as claimed in Claim 10 wherein the weight ratio is from 2:1 to 4:1.

12. A composition as claimed in any preceding Claim which comprises from 10 to 25% by weight of the polymer.

13. A composition as claimed in any preceding Claim which comprises from 5 to 88% by weight of solvating agent.

14. A composition as claimed in any preceding Claim which comprises from 2 to 70% by weight of diluting agent.

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15. A composition as claimed in any preceding claim wherein the polymer is a cellulose derivative, starch derivative, polysaccharide gum, or mixture thereof.

16. A composition as claimed in claim 15 wherein the polymer comprises xanthan gum, carboxymethyl cellulose, hydroxyethyl starch or carboxymethyl starch.

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

18. A well servicing fluid which comprises:

- (a) an aqueous medium; and
- (b) a polymer composition as claimed in any of the preceding claims.

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

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

21. A composition as claimed in any of claims 18 to 20 wherein the aqueous medium has a density greater than 1.32 g/ml.

22. A composition as claimed in claim 21 wherein the density of the aqueous medium is from 1.44 to 2.30 g/ml.

23. A method of preparing a polymer composition as claimed in any of claims 1 to 16 which comprises mixing the particulate organic polymer with the solvating agent and mixing the diluting agent with the polymer and solvating agent.



(44)

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

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