

VISCOUS HEAVY BRINES AND METHOD FOR THEIR MANUFACTURE

The present invention relates to viscous brine solutions and, more particularly, to a method of increasing the viscosity of so called heavy brines having a density greater than 1.35 g/cm^3 containing two or more of the soluble salts: calcium chloride, calcium bromide, and zinc bromide.

In recent years, the practical operating range of clear brines for use in the oil and gas industry has been significantly extended by utilizing soluble zinc salts, particularly zinc bromide, so that the advantages of clear brines can now be obtained with fluids having densities as high as 2.30 g/cm^3 at ambient temperatures and pressures.

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

Clear brines having a density of 1.70 g/cm^3 or lower are generally formulated to contain sodium chloride, sodium bromide, potassium chloride, calcium chloride, calcium bromide or mixtures of these salts. Clear brines having a density up to 1.81 g/cm^3 can be formulated with calcium chloride and calcium bromide; however, if the brine must have a low crystallization temperature, then clear brines in this density range are generally formulated to contain a soluble zinc salt. Zinc bromide is preferred because brines containing it are less corrosive than brines containing zinc chloride. Clear brines having a density greater than 1.81 g/cm^3 are formulated to contain zinc bromide.

Viscous clear fluids are sometimes desired. Generally, hydroxyethyl cellulose (HEC) and xanthan gum polymers are compatible with the fluids which do not contain

zinc salts. At higher densities, however, the hydration of the viscosifiers is significantly slower. HEC is generally considered as unsatisfactory for use in fluids containing zinc salts. However, 5 methods of activating HEC, zanthan polymers, and other water soluble polymers so that they readily hydrate in heavy brines and particularly in certain brines containing zinc bromide have been disclosed in our prior British Patent Applications No. 8101828 10 (Publication No.2070611 A); 8109880 (Publication No. 2075041 A); and 8131312.

There is still, however, a need for viscosifiers for heavy brines containing calcium chloride, calcium bromide, zinc bromide, and mixtures thereof, 15 particularly such brines containing zinc bromide in admixture with calcium chloride and/or calcium bromide.

The present invention provides a method of increasing the viscosity of a brine having dissolved 20 therein any two or all three of the salts (a) calcium chloride, (b) calcium bromide, and (c) zinc bromide, which comprises mixing the brine with a homogeneously substituted cellulose sulfate ester having from 0.3 to 1.3 sulfate groups per 25 anhydroglucose unit, but excluding
(i) mixing brines containing calcium chloride and less than 9% by weight of zinc bromide with a cellulose sulfate ester having 0.3 to 0.5 sulfate groups per anhydroglucose unit, and
30 (ii) mixing brine containing both calcium chloride and zinc bromide with a cellulose sulfate ester having 1.0 to 1.3 sulfate groups per anhydroglucose unit.

We have found that cellulose sulfate esters containing from 0.6 to 0.9 sulfate groups per anhydroglucose unit will viscosify all heavy brines containing two or more of the above-mentioned soluble salts. Those esters containing 0.3 to 0.5 sulfate groups per anhydroglucose unit will viscosify all heavy brines containing two or more of these soluble salts except those heavy brines containing calcium chloride and less than 9% by weight zinc bromide. Those esters containing 1.0 to 1.3 sulfate groups per anhydroglucose unit will viscosify all heavy brines in which the dissolved salts are calcium chloride and calcium bromide, or calcium bromide and zinc bromide.

The cellulose ester employed in accordance with this invention are preferably used in amounts from 2.5 to 15 g per 1000 cm³ of the brine.

The heavy brines for use in the present invention contain two or more soluble salts selected from calcium chloride, calcium bromide, zinc bromide, and mixtures thereof. Brines containing only calcium chloride can be formulated having a density from 1.02 to 1.40 g/cm³. Brine containing only calcium bromide can be formulated having a density from 1.02 to 1.70 g/cm³. However, because calcium chloride is much less expensive than calcium bromide, brines in the density range from 1.35 to 1.81 g/cm³ are generally formulated to contain both calcium chloride and calcium bromide, depending on the lowest temperature at which the brine will be used. Brines heavier than 1.80 g/cm³ are generally formulated to contain calcium chloride, calcium bromide, and zinc bromide, or only calcium bromide and zinc bromide depending on the lowest temperature at which the brine will be used. Brines in the density range from 1.70 to 1.80 g/cm³ may be formulated to contain calcium chloride, calcium bromide,

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and zinc bromide if brines having a lower crystallization point are desired.

5 The most difficult brines to viscosify contain zinc bromide, and these brines are preferred for use in the present invention. As indicated, such brines will have a density from 1.70 to 2.30 g/cm³.

10 Generally, brines of any density within the ranges disclosed are prepared by mixing together various standard, commercially available brines, as follows: calcium chloride brines having a density in the range from 1.32 to 1.39 g/cm³; calcium bromide brine having a density of 1.70 g/cm³ and a calcium bromide/zinc bromide brine having

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a density of 2.30 g/cm³ containing about 20% calcium bromide and about 57% zinc bromide. Solid anhydrous calcium chloride and solid calcium bromide are also used in conjunction with these brines to prepare heavy brines for use in this invention. Standard brine mixing tables are available from the various manufacturers of these brines.

The viscosifiers for use in the present invention are homogeneously substituted cellulose sulfate esters. Such cellulose esters can be prepared according to U.S. Patents No. 4,035,569 and 4,138,535. An article by Richard G. Schweiger which was published in Carbohydrate Research, Vol. 70, pp. 185-198 (1979) entitled "New Cellulose Sulfate Derivatives and Applications" describes these homogeneously substituted cellulose sulfate esters and their properties. This article discloses their potential use in drilling fluids and indicates that solutions containing these esters can be saturated with such salts as sodium or calcium chlorides.

Cellulose contains three hydroxyl groups per anhydroglucose unit at which reactions can occur to form cellulose derivatives. The average number of sulfate groups introduced into the anhydroglucose unit may, therefore, vary from slightly above 0 to 3, when all the hydroxyl groups in each anhydroglucose group have been substituted. The average number of sulfate groups introduced into each anhydroglucose unit is referred to as the degree of substitution (DS).

The homogeneously substituted cellulose sulfate esters which are useful in this invention have a DS from 0.3 to 1.3. However, all such cellulose esters are not efficient viscosifiers in all heavy brines containing two or more salts selected from calcium chloride, calcium bromide and zinc bromide. In accordance with this invention, we have found that only homogeneously substituted cellulose sulfate esters having a DS from 0.6 to 0.9 will efficiently increase the viscosity, as evidenced by a significant increase in the yield point, of all heavy brines containing

two or more of these salts. Homogeneously substituted cellulose sulfate esters having a DS from 0.3 to 0.5 efficiently increase the viscosity of all heavy brines in which the dissolved salts are 5 calcium chloride and calcium bromide, calcium bromide and zinc bromide, or all three of these salts, provided that the concentration of zinc bromide is greater than 9% by weight. Homogeneously substituted cellulose sulfate esters having a 10 DS from 1.0 to 1.3 efficiently increase the viscosity of all heavy brines containing at least two of calcium chloride, calcium bromide and zinc bromide, except those containing both calcium chloride and zinc bromide.

15 To illustrate the present invention more fully, 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 20 PROCEDURE FOR TESTING DRILLING FLUID, API RP 13B, Seventh Edition, April 1978. The physical property parameters referred to in the examples are in units expressed as follows:

25 AV = Apparent viscosity, centipoise
PV = Plastic Viscosity, centipoise
YP = Yield Point, Bars
10-Sec Gel = 10 Second Gel Strength, Bars.

Example 1

A commercially available homogeneously substituted cellulose sulfate having a DS from 0.3 to 0.5 (Colloid XHO, Stauffer Chemical Co.) was evaluated as a viscosifier
5 in various brines containing calcium chloride, calcium bromide, and zinc bromide. The cellulose sulfate was added to the brines at a concentration of 2.86 g/1000 cm³ and mixed on a Multimixer for 15 minutes. Thereafter, the brines were rolled for 16 hours at 65.5°C, cooled to room
10 temperature, and the API RP 13B rheology obtained. The data obtained are given in Table 1.

Example 2

A commercially available homogeneously substituted cellulose sulfate having a DS in the range from 0.6 to 0.9
15 (Colloid XHI, Stauffer Chemical Co.) was evaluated as a viscosifier as in Example 1. The data obtained are given in Table 2.

Example 3

A commercially available homogeneously substituted
20 cellulose sulfate having a DS from 1.0 to 1.3 (Colloid XH2, Stauffer Chemical Co.) was evaluated as a viscosifier as in Example 1. The data obtained are given in Table 3.

Comparative Example 4

A commercially available hydroxyethyl cellulose
25 (NATROSOL 250 HHR) was evaluated as a viscosifier as in Example 1. The data obtained are given in Table 4.

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TABLE 1

Evaluation of Cellulose Sulfate, D.S. = 0.3-0.5,
in Various High Density Solutions

5	Density g/cm ³	% ZnBr ₂	% CaBr ₂	% CaCl ₂	API Rheology			
					AV	PV	YP	10-Sec. Gel
	1.39 *	0	0	37.6	49	33	1.56	0.15
	1.70 *	0	53.0	0	57.5	34	2.29	0.29
	1.50 *	0	24.9	18.4	44	28	1.56	0.15
10	1.80 *	0	43.2	16.3	145	97	4.69	1.07
	1.81 *	1.7	42.5	15.8	69	53	1.56	0.15
	1.83 *	5.0	41.1	14.8	52.5	50	0.15	0.02
	1.86 *	8.4	39.8	13.9	61	62	0.39	0.15
	1.87	10.0	39.1	13.4	70	52	1.76	0.20
15	1.89	13.2	37.8	12.5	87.5	67	2.29	0.15
	1.92	16.3	36.6	11.6	111	85	2.54	-
	1.74	4.5	50.4	0	51.5	34	2.20	0.29
	1.80	11.7	46.2	0	58.5	35	2.29	-
	1.86	18.4	42.4	0	60	37	2.25	-

* Outside scope of invention

TABLE 2

Evaluation of Cellulose Sulfate, D.S. = 0.6-0.9,
in Various High Density Solutions

5	Density g/cm ³	% ZnBr ₂	% CaBr ₂	% CaCl ₂	API Rheology			10-Sec. Gel
					AV	PV	YP	
	1.39	0	0	37.6	36.5	29	0.73	0.07
	1.68	0	50.0	2.0	40.5	30	1.03	-
	1.70	0	53.0	0	46	33	1.27	0.12
10	1.50	0	24.9	18.4	32	25	0.68	0.05
	1.50	0	13.8	30.8	48	36	1.17	0.15
	1.52	0	28.6	16.0	33	26	0.68	0.05
	1.56	0	33.9	12.5	35.5	25	0.93	0.05
	1.56	0	20.6	27.4	57.5	40.5	1.66	0.15
	1.59	0	39.0	9.2	37.5	28	0.93	0.10
15	1.62	0	26.8	24.4	62	43	1.86	0.15
	1.64	0	45.4	5.0	41	31	0.98	0.10
	1.68	0	32.6	21.6	97	65	3.12	0.24
	1.74	0	38.0	19.0	126	85	4.00	0.39
	1.80	0	43.2	16.3	137	92	4.39	0.49
	1.81	1.7	42.5	15.8	122	84	3.71	0.39
20	1.83	5.0	41.1	14.8	113.5	81	3.17	0.29
	1.86	8.4	39.8	13.9	117.5	80	3.66	0.34
	1.92	16.3	36.6	11.6	111.5	76	3.47	-
	1.74	4.5	50.4	0	44	32	1.17	0.10
	1.80	11.7	46.2	0	46.5	33	1.32	-
	1.86	18.4	42.4	0	42	31	1.07	-
25	1.92	24.6	38.6	0	53	39	1.39	-
	2.04	36.0	32.1	0	61	42.5	1.78	-

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TABLE 3

Evaluation of Cellulose Sulfate, D.S. = 1.0-1.3,
in Various High Density Solutions

	5	Density g/cm ³	*	% ZnBr ₂	% CaBr ₂	% CaCl ₂	API Rheology			10-Sec. Gel
							AV	PV	YP	
		1.39	*	0	0	37.6	38.5	28	1.03	0.07
		1.70	*	0	53.0	0	40	28	1.17	0.10
		1.80		0	43.2	16.3	86	64	2.15	0.15
	10	1.81	*	1.7	42.5	15.8	52.5	52.5	0	0.10
		1.83	*	5.0	41.1	14.8	42.5	42	0.05	0.02
		1.86	*	8.4	39.8	13.9	47.5	43	0	0.05
		1.92	*	16.3	36.6	11.6	42.5	38	0.44	-
		1.74		4.5	50.4	0	40.5	28	1.22	0.15
	15	1.80		11.7	46.2	0	41	29	1.17	0.15
		1.86		18.4	42.4	0	40.5	29	1.12	0.15

* Outside Scope of Invention

TABLE 4

Evaluation of HEC in Various High Density Solutions

	Density g/cm ³	% ZnBr ₂	% CaBr ₂	% CaCl ₂	API Rheology			
					AV	PV	YP	10-Sec. Gel
5	1.39	0	0	37.6	47	31	1.51	-
	1.70	0	53.0	0	51	31	1.95	0.24
	1.80	0	43.2	16.3	127	86	4.00	-
	1.81	1.7	42.5	15.8	34	34	0	0
10	1.83	5.0	41.1	14.8	35.5	36	0	0
	1.86	8.4	39.8	13.9	31.5	31.5	0	0
	1.92	16.3	36.6	11.6	28	28	0	0
	1.74	4.5	50.4	0	7.5	7.5	0	0
	1.80	11.7	46.2	0	8.5	8.5	0	0
15	1.86	18.4	42.4	0	13.5	13.5	0	0

The data obtained indicate that HEC is not an effective viscosifier in these heavy brines containing zinc bromide. The homogeneously substituted cellulose sulfate having a DS from 0.3 to 0.5 was an effective vis-

20 cosifier in all of the heavy brines, except the brines containing less than 9% zinc bromide when calcium chloride was also present in the brine. The homogeneously substituted cellulose sulfate having a DS from 0.6 to 0.9 was an effective viscosifier in all of these heavy brines,

25 and especially in the brines which are so difficult to viscosify containing low concentrations of zinc bromide in the presence of calcium chloride. The homogeneously substituted cellulose sulfate having a DS in the range from 1.0 to 1.3 was an effective viscosifier in all of

30 the brines except all the brines containing both zinc bromide and calcium chloride. In the latter brines it performed similarly to HEC.

CLAIMS:

1. A method of increasing the viscosity of a brine having dissolved therein any two or all three of the salts (a) calcium chloride, (b) calcium bromide, and (c) zinc bromide, which comprises mixing the brine with a homogeneously substituted cellulose sulfate ester having from 0.3 to 1.3 sulfate groups per anhydroglucose unit, but excluding

(i) mixing brines containing calcium chloride and less than 9% by weight of zinc bromide with a cellulose sulfate ester having 0.3 to 0.5 sulfate groups per anhydroglucose unit, and

(ii) mixing brine containing both calcium chloride and zinc bromide with a cellulose sulfate ester having 1.0 to 1.3 sulfate groups per anhydroglucose unit.

2. A method as claimed in Claim 1 wherein the brine has a density greater than 1.70 g/cm³.

3. A method as claimed in Claim 1 or 2 wherein the brine contains calcium chloride and calcium bromide, or calcium bromide and zinc bromide, and the cellulose sulfate ester contains from 0.3 to 0.5 sulfate groups per anhydroglucose unit.

4. A method as claimed in Claim 3 wherein the brine has a density greater than 1.80 g/cm³.

5. A method as claimed in Claim 1 or 2 wherein the brine solution contains two or more soluble salts selected from calcium chloride, calcium bromide, and zinc bromide, and the cellulose sulfate ester contains from 0.6 to 0.9 sulfate groups per anhydroglucose unit.



6. A method as claimed in claim 5 wherein the brine contains all three salts.

7. A method as claimed in claim 6 wherein the brine has a density greater than 1.80 g/cm³.

5 8. A method as claimed in claim 1 or 2 wherein the brine contains calcium chloride, calcium bromide, and zinc bromide, the concentration of zinc bromide exceeding 9% by weight, and the cellulose sulfate ester contains from 0.3 to 0.5 sulfate groups per anhydroglucose
10 unit.

9. A method as claimed in claim 8 wherein the density of the brine is greater than 1.86 g/cm³.

10. A method as claimed in any preceding claim which comprises adding 2.5 to 15 grams of cellulose ester
15 per 1000 cm³ of brine.

11. A method as claimed in claim 1 and substantially as hereinbefore described.

12. A brine having dissolved therein (1) any two or all three of the salts (a) calcium chloride, (b) calcium
20 bromide, and (c) zinc bromide, and (2) a homogeneously substituted cellulose sulfate ester having from 0.3 to 1.3 sulfate groups per anhydroglucose unit, but excluding
(i) brines containing calcium chloride and less than 9% by weight of zinc bromide when the cellulose sulfate ester
25 has 0.3 to 0.5 sulfate groups per anhydroglucose unit, and
(ii) brines containing both calcium chloride and zinc bromide when the cellulose sulfate ester has 1.0 to 1.3 sulfate groups per anhydroglucose unit.

13. A brine as claimed in claim 12 having a density
30 of at least 1.70 g/cm³.



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14. A brine as claimed in claim 12 or 13 which comprises from 2.5 to 15 grams per liter of the cellulose ester.

15. A brine as claimed in any of claims 12 to 14 which comprises calcium chloride and calcium bromide or calcium bromide and zinc bromide.

16. A brine as claimed in any of claims 12 to 14 which contains calcium chloride, calcium bromide, and zinc bromide, and the cellulose sulfate ester has from 0.6 to 0.9 sulfate groups per anhydroglucose unit.

17. A brine as claimed in claim 16 having a density greater than 1.80 g/cm^3 .

18. A brine as claimed in any of claims 12 to 14 which contains calcium chloride, calcium bromide, and zinc bromide, the concentration of zinc bromide being greater than 9% by weight, and the cellulose sulfate ester having from 0.3 to 0.5 sulfate groups per anhydroglucose unit.

19. A brine as claimed in claim 18 having a density greater than 1.86 g/cm^3 .

20. A brine as claimed in claim 12 and substantially as hereinbefore described.
