

DEFOAMERS FOR AQUEOUS LIQUIDS CONTAINING SOLUBLE ZINC SALTS

The present invention relates to defoaming compositions for aqueous liquids containing a soluble zinc salt, and more particularly to defoaming compositions for so called heavy brines having a density of 1.70 g/cm^3 .

5 In recent years, the practical operating range of clear brines for use in the oil and gas industry has been significantly extended by utilising 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
10 temperatures and pressures.

The high density clear brines are extensively used, 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
15 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 are generally
20 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 1.82 g/cm^3 can be formulated with calcium chloride and calcium bromide. If the brine must have a low crystallisation temperature, however, then clear
25 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 1.82 g/cm^3 are formulated to contain zinc bromide.

30 Viscous clear fluids are sometimes desired. Generally, hydroxyethyl cellulose (HEC) and xanthan gum (XC) polymers are compatible with the fluids which do not contain zinc salts. At the higher densities, however, the hydration

of the viscosifiers is significantly slower. HEC is generally considered as unsatisfactory for use in fluids containing zinc salts. Methods of activating HEC, XC polymer, and other water soluble polymers such that they readily hydrate
5 in heavy brines containing zinc bromide have been disclosed in our prior British Patent Applications No. 8101828 (Publication No. 2070611 A), No. 8109880 (Publication No. 2075041 A), No. 8125937 (Publication No. 2086923 A) and No. 8131312.

10 It has been found that clear heavy brines containing soluble zinc salts foam upon mixing. In the presence of a hydrophilic polymer viscosifier such as HEC, the foam is stabilized to the extent that an excessive aging time is required to allow the foam to break and be eliminated.

15 It is an object of the present invention to provide a new composition which is useful for eliminating the formation of a stable foam in heavy brines containing a soluble zinc salt.

It is another object of this invention to provide a
20 method of eliminating the formation of a stable foam in heavy brines containing a soluble zinc salt.

Still another object of this invention is to provide improved heavy brine well servicing fluids.

A further object is to provide improved viscous heavy
25 brine well servicing fluids.

This invention provides a defoaming composition comprising a mixture of 2,6,8-trimethyl-4-nonanone and the triethoxylated derivative of 2,6,8-trimethyl-4-nonanol.

This invention also provides a method of decreasing
30 the foam which forms on mixing an aqueous brine containing a soluble zinc salt which comprises mixing the above-described defoaming composition with the brine.

This invention further provides a heavy brine well servicing composition which comprises an aqueous solution
35 having a density greater than 1.70 g/cm^3 and the above defined defoaming composition.

The present invention is based on the discovery that

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blends of 2,6,8-trimethyl-4-nonanone (TMN) and the triethoxylated derivative of 2,6,8-trimethyl-4-nonanol (TETMN) synergistically interact to decrease the foaming in heavy brines containing a soluble zinc salt, particularly zinc bromide.

The volume ratio of TETMN to TMN in the defoaming composition should be from 9:1 to 1:9, preferably from 7:1 to 1:7, and most preferably from 5:1 to 1:5.

The concentration of the defoaming composition used to prevent foaming or to eliminate the foam from heavy brines containing a soluble zinc salt need only be an effective amount, generally from 0.06 to 31.5 cm³ per cubic metre of brine, preferably from 0.3 to 3.2 cm³/m³.

The heavy brines in which the TMN and TETMN interact synergistically to decrease foaming may contain from 1 to 60% by weight of a soluble zinc salt, preferably zinc bromide. The remaining soluble salts in the heavy brines are generally calcium chloride and/or calcium bromide. Preferably the heavy brine will contain at least 16% by weight of zinc bromide, most preferably at least 20% by weight of zinc bromide.

It is preferred that the heavy brines of this invention containing a foam eliminating amount of the defoaming composition of this invention also contain a hydrophilic polymer hydrated therein, particularly hydroxyethyl cellulose (HEC). Most preferably the hydroxyethyl cellulose shall have been activated for use in heavy brines containing zinc bromide, such as by the methods disclosed in the copending patent applications referred to above. The HEC will generally be present in a concentration of from 2.86 to 14.3 g/l.

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To illustrate more fully the present invention, the following non-limiting Examples are presented. Unless otherwise indicated, all percentages are weight percentages and 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:

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AV = apparent viscosity, centipoise

PV = plastic viscosity, centipoise

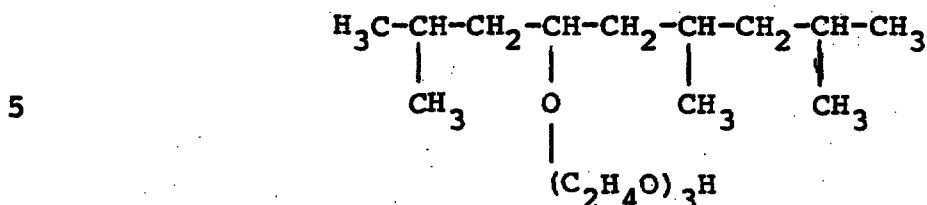
YP = yield point, kg/m²

gel strength = kg/m²

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Example 1

Various blends of 2,6,8-trimethyl-4-nonanone (TMN) and triethoxylated 2,6,8-trimethyl-4-nonanol (TETMN),



were prepared by mixing. These blends were evaluated as defoamers as follows: (1) 350 milliliters of brine were mixed with 7.5 grams of an activated hydroxyethyl cellulose gellant
 10 composition containing 20% by weight of NATROSOL 250 HHR hydroxyethyl cellulose, 25% by weight of glycerol, 0.4% by weight of CAB-O-SIL MS fumed silica, and 54.6% by weight of isopropanol for 5 minutes on a Multimixer; (2) after 4 minutes mixing there were added the defoamer blends listed in
 15 Table 1; (3) immediately after mixing the brines were poured into graduated cylinders; (4) the height of foam was noted and thereafter observed at one minute intervals; and (5) the test was terminated after 5 minutes if the foam had not dissipated. Two brines were used having the following pro-
 20 perties:

Brine A - 2.05 g/cm³ containing 7.15% by weight calcium chloride, 30.2% by weight of calcium bromide, and 32% by weight of zinc bromide in water.

25 Brine B - 2.30 g/cm³ containing 20% by weight of calcium bromide and 57% by weight of zinc bromide in water.

The observed time for foam elimination is given in Table 1.

The data indicate that the TETMN and TMN synergistically reduced the time required for foam elimination.

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Table 1

BLEND NUMBER	VOLUME RATIO TETMN TMN	VOLUME OF BLEND ml	EQUIVALENT VOLUME OF TETMN ml	EQUIVALENT VOLUME OF TMN ml	MINUTES FOR FOAM ELIMINATION	
					BRINE A	BRINE B
-	-	-	0.20	0	5	4
-	-	-	0.10	0	4	4
-	-	-	0	0.20	2	2
-	-	-	0	0.10	2	3
-	-	-	0	0.05	4	4
-	-	-	0	0.025	1	2
1	7/1	0.20	0.175	0.05	0	1
2	3/1	0.20	0.15	0.10	0	1
3	1/1	0.20	0.10	0.15	0	1
4	1/3	0.20	0.05	0.175	1	3
5	1/7	0.20	0.025	0.05	0	2
6	1/1	0.10	0.05	0.025	0	2
7	1/1	0.05	0.025	0.025	0	2

Example 2

A 1/1 blend of TMN and TETMN was evaluated for its effect on the rheological properties of this brine, viscosified with HEC, as follows: (1) viscosified brines were prepared containing 350 milliliters of Brine A or Brine B, 7.5 grams of gellant A or gellant B, and 0.20 grams of the 1/1 blend by mixing on a Multimixer for 5 minutes and rolling the brines in a roller oven at room temperature for sixteen hours; (2) the rheological properties were obtained; (3) the viscosified brines were rolled at 65.5°C for 16 hours; and (4) the rheological properties were obtained after cooling to room temperature. The data obtained are given in Table 2. Gellant A contains 20% by weight of NATROSOL 250 HHR hydroxyethyl cellulose, 25% by weight of glycerol, 0.4% by weight of CAB-O-SIL M5 fumed silica, and 54.6% by weight of isopropanol. Gellant B contains 20% by weight of NATROSOL 250 HHR, 22% by weight of 0.25N NaOH, and 58% by weight of isopropanol.

The data indicate that this defoamer blend had no deleterious effect on the rheological properties of this brine.

Table 2

DEFOAMER BLEND g/litre	GELLANT	BRINE	TEMP. OF ROLLING	API RHEOLOGICAL CHARACTERISTICS			
				AV	PV	YP	GEL STRENGTHS 10 Sec. 10 Min.
NONE	A	A	R.T.	44.5	41	0.34	0.05 0.05
0.57	A	A	R.T.	46.5	43	0.34	0.05 0.05
NONE	A	A	65.5°C	170a	-	-	0.78 0.78
0.57	A	A	65.5°C	170a	-	-	0.78 0.78
NONE	A	B	R.T.	b	-	-	1.86 1.95
0.57	A	B	R.T.	b	-	-	1.66 1.76
NONE	A	B	65.5°C	216a	-	-	1.76 1.81
0.57	A	B	65.5°C	207a	-	-	1.66 1.66
NONE	B	A	R.T.	84.5	66	1.81	0.20 0.20
0.57	B	A	R.T.	84.5	67	1.71	0.15 0.15
NONE	B	A	65.5°C	254a	-	-	1.46 1.66
0.57	B	A	65.5°C	262a	-	-	1.56 1.66
NONE	B	B	R.T.	129.5	81	4.74	1.07 1.07
0.57	B	B	R.T.	127	82	4.39	0.93 0.93
NONE	B	B	65.5°C	219a	-	-	1.27 1.27
0.57	B	B	65.5°C	222a	-	-	1.27 1.27

a = 300 rpm reading
b = >150, too viscous to measure
R.T. = Room Temperature



CLAIMS:

1. A defoaming composition comprising a mixture of 2,6,8-trimethyl-4-nonanone and the triethoxylated derivative of 2,6,8-trimethyl-4-nonanol.
- 5 2. A composition as claimed in claim 1 wherein the volume ratio of 2,6,8-trimethyl-4-nonanone to the triethoxylated derivative of 2,6,8-trimethyl-4-nonanol is from 9:1 to 1:9.
- 10 3. A composition as claimed in claim 2 wherein the volume ratio is from 7:1 to 1:7.
4. A composition as claimed in claim 2 or 3 wherein the volume ratio is from 5:1 to 1:5.
- 15 5. A composition as claimed in claim 1 and substantially as hereinbefore described with reference to either of the Examples.
- 20 6. A method of decreasing the foam which forms on mixing an aqueous brine containing a soluble zinc salt which comprises mixing with the brine a defoaming composition as claimed in any preceding claim.
- 25 7. A method as claimed in claim 6 wherein the zinc salt is zinc bromide.
8. A method as claimed in claim 7 wherein the brine has a density greater than 1.702 g/cm^3 and contains at least
30 20% by weight of zinc bromide.
9. A heavy brine well servicing fluid which comprises an aqueous solution having a density greater than 1.70 g/cm^3 and a defoaming composition as claimed in any of
35 claims 1 to 4.



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10. A heavy brine well servicing fluid as claimed in claim 9 which comprises the aqueous solution having a density greater than 1.702 g/cm^3 , from 2.86 to 14.3 g/litre of hydroxyethyl cellulose, and from 0.06 to $31.5 \text{ cm}^3/\text{m}^3$ of the defoaming composition.

11. A well servicing fluid as claimed in claim 10 which comprises from 0.3 to $3.2 \text{ cm}^3/\text{m}^3$ of the defoaming composition.

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