

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 December 2007 (13.12.2007)

PCT

(10) International Publication Number
WO 2007/143489 A2

(51) International Patent Classification:
C08K 5/15 (2006.01)

(21) International Application Number:
PCT/US2007/070051

(22) International Filing Date: 31 May 2007 (31.05.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/444,722 1 June 2006 (01.06.2006) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COMPOSITION FOR INHIBITING FORMATION OF GAS HYDRATES

(57) Abstract: A composition for preventing or retarding the formation of gas hydrates or for reducing the tendency of gas hydrates to agglomerate, during the transport of a fluid comprising water and a hydrocarbon, through a conduit, comprising, (a) a polymer which is a homopolymer of N-vinyl caprolactam, or a copolymer of N-vinyl caprolactam, with a comonomer, e.g. N,N-dialkyl-aminoethyl(meth)acrylate, and (b) a synergistic additive therewith which is a cationic or non-ionic surfactant, or a sugar, and mixtures thereof.



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COMPOSITION FOR INHIBITING FORMATION OF GAS HYDRATES

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of U.S. Nonprovisional Application Serial No. 11/444,722, filed on June 1, 2006, which is incorporated herein by reference thereto.

FIELD OF THE INVENTION

This invention relates to a composition for preventing or retarding the formation of gas hydrates, or for reducing the tendency of such hydrates to agglomerate during the transport of a fluid comprising water and a hydrocarbon through a conduit, and, more particularly, to a composition of a vinyl caprolactam polymer and synergistic additive therewith.

BACKGROUND OF THE INVENTION

It is well known in the art that formation of gas hydrates in a conduit, e.g. a pipeline, during the transport of liquids, such as oil, and gases, particularly lower hydrocarbons, e.g. methane, ethane, propane, butane and iso-butane, is a serious problem, especially in areas with a low temperature in the winter season or in the sea. Generally these temperatures are so low that gas hydrate formation occurs in the wells, due to the presence of water unless special steps are taken. For example, insulation around the pipe will decrease the chance of gas hydrate formation; however, if the field is relatively small or far away from the production platform, the costs of using such insulation are too high to make it an economically attractive option. It is also known to add anti-freeze compounds, for example, glycol or methanol, during transport to minimize gas hydrate formation; however, very large quantities of these compounds can be required to be effective.

Representative of the prior art in this field are the following U.S. patents: U.S. 4,915,176; 5,420,370; 5,432,292; 5,723,524; 5,741,758; 5,874,660; 6,028,233; 6,093,863; 6,096,815; 6,117,929; and 6,180,699; as well as EPA 0526929A1; EPO 0323774A1; Can. Pat. Appln 2,073,577; WO 93/25798; WO 95/17579; Gas Hydrates

and Hydrate Prevention 73 GPA Annual Convention, pgs 85-93; WO 96/08456; WO 96/08636; WO 93/25798; EPA 0457375A1 and WO 94/12761.

SUMMARY OF THE INVENTION

What is described herein is a composition for preventing or retarding the formation of gas hydrates or for reducing the tendency of gas hydrates to agglomerate, during the transport of a fluid comprising water and a hydrocarbon, through a conduit, comprising, (a) a homopolymer of N-vinyl caprolactam, or a copolymer of N-vinyl caprolactam and a comonomer which is an N,N-dialkylaminoethyl(meth)acrylate, and (b) a synergistic additive therewith which is a cationic or non-ionic surfactant, or a sugar, and mixtures thereof.

Preferably the polymer is made in a suitable solvent, e.g. a low molecular weight glycol ether containing an alkoxy group having at least 3 carbon atoms, most preferably, butoxy ethanol, as described in U.S. Patents 6,180,699, 6,096,815, 6,093,863 and 5,723,524.

In one embodiment of the invention, the composition includes (a) a homopolymer of polyvinyl caprolactam.

In another embodiment, (a) is a copolymer of vinylcaprolactam and diethylaminoethyl methacrylate.

Suitably (b) is a non-ionic surfactant, preferably a C₂-C₈ N-alkyl pyrrolidone, linear or cyclic, e.g. N-ethyl pyrrolidone, N-octyl pyrrolidone, or N-cyclohexyl pyrrolidone, and most preferably, N-octyl pyrrolidone.

In other embodiments of the invention, (b) is sorbitol, mannitol, fructose and/or sucrose.

In another embodiment, of the invention, (b) is a non-ionic surfactant which includes poly(ethylene glycol) and poly(ethylene oxide-propylene oxide).

These and other features of the invention will be made apparent from the following description thereof.

DETAILED DESCRIPTION OF THE INVENTION

The composition of the invention includes a homopolymer of vinyl caprolactam and copolymers of vinyl caprolactam, preferably an N,N-dialkyl aminoalkyl methacrylamide, e.g. N,N-dimethylamino propyl methacrylamide; N,N-dialkyl aminoalkyl (meth)acrylate; e.g. N,N-dimethylaminoethyl (meth)acrylate, and quaternized salts thereof, e.g. N-alkyl bromides; and N-alkyl chlorides; and the like.

Preferably the polymer is made in a suitable solvent e.g. BGE, and maintained therein in the composition of the invention as disclosed in U.S. Patents 5,723,524, 6,093,863, 6,096,815, and 6,180,699. Less preferably, they are made in another solvent, such as isopropanol solvent, the solvent removed, and the desired glycol ether solvent added. Preferred polymers are low weight average molecular weight polymers, e.g., less than 10,000, preferably less than 7,000.

Suitable solvents include low molecular weight glycol ethers containing an alkoxy group having at least 3 carbon atoms, N-methylpyrrolidone (NMP), ethylene glycol, water and blends thereof. Representative glycol ethers include 2-butoxyethanol (ethylene glycol monobutyl ether); propylene glycol butyl ether; (diethylene glycol) monobutyl ether; and 2-isopropoxy-ethanol. 2-Butoxyethanol (BGE) is preferred.

Preferred formulations of the invention include: Polymer (made in BGE solvent), BGE solvent, synergist additive, and optionally, a second solvent, (e.g. ethylene glycol) corrosion inhibitor and water.

Compositions of Invention:

Polymer	0.01-55% suitable
	1.0-40% preferred
	5-30% optimum
	In suitable solvent
Synergistic additive	0.001-10% suitable
	0.01-5% preferred
	0.1-3% optimum

Second Solvent	0-70% suitable
	2-50% preferred
	5-25% optimum

USE RANGES

The composition of the invention, once prepared, is used to treat natural gas containing water at a suitable use rate of 0.05–15 wt.% based on water content, preferably 0.1–10 wt.%, and, optimally 0.20–6 wt.%.

EXPERIMENTAL

Equipment

The gas hydrate inhibition tests were conducted in a 500 ml, 316 stainless steel autoclave vessel (hereafter referred to as a "rig") having a usable volume of 200 ml, equipped with a thermostated cooling jacket, sapphire window, platinum resistant thermometer (PRT), inlet and outlet, and magnetic stirring pellet. The rig was rated up to 400°C and down to -25°C. Temperature and pressure were data logged, while cell content was visually monitored by a boroscope video camera connected to a time lapsed video recorder. Hydrate formation in the rig was detected using a combination of three methods: visual detection of hydrate crystals, decrease in vessel pressure due to gas uptake and by the temperature exotherm created by heat released during hydrate formation.

Preparation of Polymer

EXAMPLE

300 g. of 2-butoxyethanol was charged into a 1-liter resin reaction fitted with a propeller agitator, a reflux condenser, a nitrogen inlet tube and a thermowatch, and heated to 150°C. A monomer pre-mix was prepared by mixing 200 g. of vinyl caprolactam with 4.00 g of di-t-butyl peroxide initiator in a 400-ml beaker. Then the monomer pre-mix was pumped into the reaction kettle over a period of 2 hours. The reaction mixture then was held at 150°C for 1.5 hours before adding 0.50 g of di-t-butyl peroxide initiator, and held at 150°C for an additional 3 hours. After cooling to room temperature, the product was a light brown, viscous poly(vinyl caprolactam)

(PVCL) in 2-butoxyethanol (BGE) at 40% solids. Residual vinyl caprolactam was 0.9% by GC analysis. The PVCL polymer had a relative viscosity of 1.074 (1% in 2-butoxyethanol), a GPC molecular weight of 1,210 (polyethylene glycol standard), and a cloud point of 42°C.

Performance Tests

The performance tests were carried out using distilled water as the aqueous phase.

(1) Blank Tests

Blank tests were performed at a prescribed pressure, e.g. 75, 100 or 125 bar, and at a temperature of 4°C (subcooling = ~10 – 12.5°C). The high water cut mixture was stirred continuously until a hydrate formed.

(2) Invention Tests

The same tests as described for the blanks were run using various levels of each composition of the invention. The treat rate of the composition was expressed as a “wt% level” based on the water cut.

Data logging was started. The rig was then pressurized to the selected pressure with the test gas and the temperature of the thermostat was set at 4°C. The contents in the rig were then stirred for 48 hours. Throughout the tests, both temperature and pressure were monitored. The rig content was visually monitored by a boroscope video camera.

The test results are shown in Tables 1-3 below. Table 1 shows the results using P(VCL) alone or with octyl pyrrolidone LP-100 as the inhibitor.

TABLE 1

Sample	Use Rate Wt% Polymer	Wt% Additive	Induction time (min)		Final Pressure (bar)		Results
			Rig 1	Rig 2	Rig 1	Rig 2	
Blank – DI water*	-	-	2		24		hard hydrates
P(VCL)** high MW	1.0% in ethanol	--	2		62		foam, soft hydrates
P(VCL)** high MW	1.0% in methanol	--		480		58	foam, hydrates

Sample	Use Rate Wt% Polymer	Wt% Additive	Induction time (min)		Final Pressure (bar)		Results
			Rig 1	Rig 2	Rig 1	Rig 2	
--***	--	0.1% LP-100	60	100	64	51	soft hydrates
P(VCL)***	1.50% in BGE	0.1% LP-100	175		42		foam, soft hydrates
P(VCL)***	1.5% Formulation 1	--	225	130	58	61	hard hydrates
P(VCL)***	1.5% Formulation 1	0.1% LP-100	150	1400	49	71	no hydrates
P(VCL)***	3.0% Formulation 1	0.1% LP-100		2880		71	no hydrates
P(VCL)	1.0% Formulation 1	--	>22,000	>22,000	30	30	no hydrates

* initial pressure – 50 bar

** initial pressure – 75 bar

*** initial pressure – 100 bar

Tables 2 and 3 shows the results using a copolymer of P(VCL) and N,N-dimethyl aminoethyl methacrylate (DEAEMA) as the comonomer, alone or with octyl pyrrolidone, to reduce hydrate formation.

TABLE 2

Sample	Use Rate Wt% Polymer	Wt% Additive	Induction time (min)		Final Pressure (bar)		Results
			Rig 1	Rig 2	Rig 1	Rig 2	
P(VCL/DEAEMA)	1.0% Formulation 2	*	524	2	53	27	hard, solid hydrates
P(VCL/DEAEMA)	2.5% Formulation 2	*	290		59		hard, hydrates
P(VCL/DEAEMA)	3.0% Formulation 2	*	650		61		hard, solid hydrates
	--	0.1% LP-100*		60		65	very soft hydrates
		0.05% LP-100*		1		63	very soft hydrates
Blank	-	*	4	7	47	42	solid hydrate

Sample	Use Rate Wt% Polymer	Wt% Additive	Induction time (min)		Final Pressure (bar)		Results
			Rig 1	Rig 2	Rig 1	Rig 2	
P(VCL/DEAEMA)	3.0% Formulation 2	0.1% LP- 100***	2800	2880	87	74	no hydrates
P(VCL/DEAEMA)	3.0% Formulation 2	0.05% LP- 100***		3050		78	foam, minimal hydrates
P(VCL/DEAEMA)	1.0% Formulation 2	--	>20,000	>20,000	30	30	no hydrates

* initial pressure – 75 bar

*** initial pressure – 100 bar

Table 3 show the test results using P(VCL/DEAMA) copolymer alone, or with a synergistic additive therewith. The results show the efficacy of the composition of the invention in reducing hydrate formation.

TABLE 3

Sample	Use Rate Wt% Polymer	Wt% Additive	Induction time (min)		Final Pressure (bar)		Results
			Rig 1	Rig 2	Rig 1	Rig 2	
P(VCL/DEAEMA)*	1.0% in Formulation 2	--		524		53	hard hydrates
P(VCL/DEAEMA)*	2.5% in Formulation 2	--	290		59		hard hydrates
P(VCL/DEAEMA)*	1.5% in Formulation 2	0.5% sorbitol		1440		75	no hydrates
P(VCL/DEAEMA)*	1.50%	0.5% glycerol	2	15	56	61	foam, soft hydrates
P(VCL/DEAEMA)*	2.50%	0.5% glycerol		370		60	hydrate chunks
P(VCL/DEAEMA)*	2.50%	0.5% propylene glycol		730		62	hard hydrates
P(VCL/DEAEMA)*	1.50%	0.5% sorbitol	1440		70		no hydrates
P(VCL/DEAEMA)*	1.50%	1.0% sorbitol		1440		75	no hydrates
P(VCL/DEAEMA)*	1.50%	1.0% mannitol	1480		74		no hydrates
P(VCL/DEAEMA)*	2.50%	0.5% sorbitol	1440		70		no hydrates
P(VCL/DEAEMA)***	1.50%	1.5% sorbitol		2000		84	small amount hydrates

Sample	Use Rate Wt% Polymer	Wt% Additive	Induction time (min)		Final Pressure (bar)		Results
			Rig 1	Rig 2	Rig 1	Rig 2	
P(VCL/DEAEMA) ^{***}	1.5% in Formulation 2	0.5% sorbitol		1280		87	soft hydrates
P(VCL/DEAEMA) ^{***}	1.5% in Formulation 2	0.5% sorbitol		1440		75	no hydrates
P(VCL/DEAEMA) ^{***}	1.5% in Formulation 2	1.5% sorbitol	2600	2880	82	91	some soft hydrates

* initial pressure – 75 bar

*** initial pressure – 100 bar

The compositions of the invention exhibit improved kinetic hydrate inhibition at elevated pressures.

While the invention has been described with particular reference to certain embodiments thereof, it will be understood that changes and modifications may be made which are within the skill of the art.

CLAIMS

WHAT IS CLAIMED IS:

1. A composition for preventing or retarding the formation of gas hydrates or for reducing the tendency of gas hydrates to agglomerate, during the transport of a fluid comprising water and a hydrocarbon, through a conduit, comprising, (a) a homopolymer of N-vinyl caprolactam, or a copolymer of vinyl caprolactam with an N,N-dialkylaminoethyl(meth) acrylate and quats thereof, and mixtures thereof and (b) a synergistic additive therewith which is a cationic or non-ionic surfactant, or a sugar, and mixtures thereof.
2. A composition according to claim 1 which includes a solvent which is a low molecular weight glycol ether containing an alkoxy group having at least 3 carbon atoms.
3. A composition according to claim 2 wherein (a) said homopolymer is polyvinyl caprolactam made in butoxyethanol.
4. A composition according to claim 2 wherein (a) said copolymer is polyvinyl(caprolactam)/diethylaminoethyl methacrylate made in butoxyethanol.
5. A composition according to claim 1 wherein (b) said non-ionic surfactant is a C₂-C₈ N-alkyl pyrrolidone, linear or cyclic, e.g. N-ethyl pyrrolidone, N-octyl pyrrolidone, or N-cyclohexyl pyrrolidone.
6. A composition according to claim 1 wherein (b) said non-ionic surfactant is N-octyl pyrrolidone.
7. A composition according to claim 1 wherein (b) is sorbitol, mannitol, fructose and/or sucrose.
8. A composition according to claim 1 wherein (b) said non-ionic surfactant is poly(ethylene glycol), or polyethylene oxide-propylene oxide.