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An agency of Industry Canada

CA 2387420 C 2009/09/29

(11)(21) 2 387 420

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 2000/07/13
(87) Date publication PCT/PCT Publication Date: 2001/04/19
(45) Date de délivrance/Issue Date: 2009/09/29
(85) Entrée phase nationale/National Entry: 2002/04/10
(86) N° demande PCT/PCT Application No.: US 2000/018987
(87) N° publication PCT/PCT Publication No.: 2001/027055
(30) Priorités/Priorities: 1999/10/12 (US09/416,307);
1999/10/12 (US09/415,657)

(51) Cl.Int./Int.Cl. *C07C 7/20* (2006.01),
C08L 39/04 (2006.01), *C08L 39/08* (2006.01),
C09K 15/30 (2006.01)

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(54) Titre : INHIBITION DE LA CORROSION ET D'HYDRATES DE GAZ LORS DU TRANSPORT D'EAU ET D'HYDROCARBURES DANS UN PIPELINE

(54) Title: CORROSION AND GAS HYDRATE INHIBITION DURING TRANSPORT OF WATER AND A HYDROCARBON THROUGH A PIPELINE

(57) Abrégé/Abstract:
What is described herein is a process of corrosion and gas hydrate inhibition of a steel pipeline during transport of water and gas, or water and an oil, or mixtures thereof, therethrough, including introducing a copolymer of vinyl caprolactam and vinylpyridine into said pipeline.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 April 2001 (19.04.2001)

PCT

(10) International Publication Number
WO 01/27055 A1

(51) International Patent Classification[7]: C07C 7/20

(21) International Application Number: PCT/US00/18987

(22) International Filing Date: 13 July 2000 (13.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

09/415,657	12 October 1999 (12.10.1999)	US
09/416,307	12 October 1999 (12.10.1999)	US

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(81) Designated States *(national)*: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search 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.

WO 01/27055 A1

(54) Title: CORROSION AND GAS HYDRATE INHIBITION DURING TRANSPORT OF WATER AND A HYDROCARBON THROUGH A PIPELINE

(57) Abstract: What is described herein is a process of corrosion and gas hydrate inhibition of a steel pipeline during transport of water and gas, or water and an oil, or mixtures thereof, therethrough, including introducing a copolymer of vinyl caprolactam and vinylpyridine into said pipeline.

CORROSION AND GAS HYDRATE INHIBITION DURING TRANSPORT OF WATER AND A HYDROCARBON THROUGH A PIPELINE

This invention relates to a process of corrosion inhibition of a steel pipeline during transport of water and gas, or water and oil, or mixtures thereof, therethrough. Furthermore it relates to a composition for preventing or retarding the formation of gas hydrates during the transport of a fluid comprising water and a hydrocarbon through a conduit.

U.S. Pat. 4,174,370 described the use of certain pyridine compounds for inhibiting the corrosion of metals, particularly the prevention of corrosion of pipe which is on contact with a corrosive oil-containing medium, as, for example, in oil wells producing corrosive oil or oil-brine mixtures.

U.S. Pat. 5,723,524 describes compositions for retarding the formation of gas hydrates in a gas/water system.

It is well known in the art that the formation of gas hydrates in a conduit, e.g. in a pipeline, where an aqueous phase is inherently present, during the transport of liquids such as oil, and of gases, particularly lower hydrocarbons, e.g. methane, ethane, propane, butane, isobutane and natural gas, is a serious problem, especially in areas with a low temperature in the winter season or in the sea. Generally, the ambient temperatures in such areas are so low that gas hydrates are formed in the gas transportation pipeline, due to the inevitable presence of co-produced water therein. Insulation of the pipelines may decrease the opportunity for gas hydrate formation; however, if the field is relatively small and some distance from the production facilities, the cost of providing suitable insulation is too high to make such a field economically attractive. It is also known to add anti-freeze

compounds, for example, ethylene glycol or methanol, during transport of such liquids and gases to minimize gas hydrate formation; however, large quantities of these highly flammable compounds are required to be effective which is expensive and unsafe.

Representative of the prior art in this field are U.S. Pats. 4,915,176; 5,420,370; 5,432,292; and 5,723,524; EPO 0323774A1; EPA 0457375A1; EPA 0526929A1; Can. Pat. Appln. 2,073,577; "Gas Hydrates and Hydrate Prevention", 73 GPA Annual Convention, pages 85-93; WO 96/08456; WO 96/08636; WO 93/25798; WO 94/12761; WO 95/17579; and WO 95/32356.

SUMMARY OF THE INVENTION

In one aspect, the invention provides a composition for preventing or retarding the formation of a gas hydrate or for reducing the tendency of a gas hydrate to agglomerate during the transport of a fluid comprising water and a hydrocarbon, through a conduit, comprising a copolymer of (a) vinyl caprolactam and (b) vinyl pyridine.

In a further aspect, the invention provides a single phase composition for preventing or retarding the formation of a gas hydrate or for reducing the tendency of a gas hydrate to agglomerate, during the transport of a fluid comprising water and a hydrocarbon, through a conduit, where an aqueous phase is inherently present, comprising (a) a solution of a copolymer of vinyl caprolactam and a vinyl pyridine having a molecular weight in the range of about 500 to 2500, GPC, polyethylene glycol standard, made in (b) a polymerization solvent which is a glycol ether containing an alkoxy group having at least 3 carbon atoms, and including (c) a carrier solvent.

What is described herein is a single phase composition for effectively inhibiting the corrosion of pipeline conduits, and for preventing or retarding the formation or agglomeration of gas hydrates, during the transport of a fluid comprising water and a hydrocarbon, through the conduit. The composition comprises a copolymer of (a) vinyl caprolactam and (b) vinyl pyridine; optionally, a terpolymer with vinyl pyrrolidone, preferably wherein the vinyl pyridine is the 2- or 4-vinyl pyridine, optionally quaternized, e.g. with a C_1-C_{18} alkyl halide, e.g. the iodide, bromide, chloride or fluoride; having a cloud point of >10°C, preferably >15°C.

Most preferably, the composition is made in a polymerization solvent which is a glycol ether, containing an alkoxy group having at least 3 carbon atoms, and most preferably, which is 2-butoxyethanol (BGE); and includes also a carrier solvent different from the polymerization solvent, preferably, monoethylene glycol (MEG).

In a preferred embodiment of the invention, the vinyl caprolactam monomer comprises about 70-97% of the polymer, and has a molecular weight of about 500 to 2500.

CORROSION INHIBITION

This function of this invention relates to the use of the copolymer in inhibiting the corrosion of metals, most particularly iron, steel and ferrous alloys. These copolymer compounds can be used in a wide variety of applications and systems where iron, steel and ferrous alloys are affected by corrosion. They may be employed for inhibiting corrosion in processes which require a protective or passivating coating as by dissolution in the medium which comes in contact with the metal. They can be used in preventing atmospheric corrosion, underwater corrosion, corrosion in steam and hot water systems, corrosion in chemical industries, underground corrosion, etc.

The polymer which exhibits advantageous dual corrosion and gas hydrate inhibitory characteristics in the composition of the invention is a copolymer of about 70-97% by weight of vinyl caprolactam and 3-25% by weight of vinyl pyridine, preferably the 2- and 4-vinyl pyridine compounds, and, optionally, terpolymers with up to 15% by weight of vinyl pyrrolidone therein.

Preferably the vinyl caprolactam monomer comprises about 75-95% of the polymer and the vinyl pyridine monomer is present in an amount of about 5-15%; optionally, vinyl pyrrolidone is included therein in an amount of up to 10%.

The polymers of the invention also may be quaternized, suitably with about a C_1-C_{18} alkyl halide; e.g. an alkyl iodide.

Preferably the polymer has a molecular weight of about 500 to 2500.

The composition herein is a single phase system having a cloud point of >10°C, preferably >15°C.

Preferably, the polymer is synthesized from its monomers in a polymerization solvent which preferably is a glycol ether containing an alkoxy group having at least 3 carbon atoms. Representative of such suitable glycol

ethers are 2-butoxyethanol (ethylene glycol monobutyl ether); propylene glycol butyl ether; (diethylene glycol) monobutyl ether; and 2-isopropoxy-ethanol. 2-Butoxyethanol (BGE) is most preferred.

The product of the polymerization is a composition of the polymer in its polymerization solvent, e.g. BGE. Generally, the weight ratio of the polymerization solvent to the polymer is about 1:1.5 to 3:3 to 1, preferably about 1.5:1.

The composition is then provided with a suitable carrier solvent such as monoethylene glycol (MEG), methanol, ethanol, propanol, 1,4-butanediol, butanol, pentanol, hexanol, cyclohexyl pyrrolidone, propargyl alcohol, N-methylpyrrolidone and the like, preferably MEG. Suitably, the concentration of MEG in the aqueous phase, i.e. under pipeline inhibition conditions, is about 2.5-10 wt. %, preferably 4-5 wt. %.

The thus-formed solution with carrier solvent can be further diluted with a dilution liquid, preferably water or methanol, or mixtures thereof, if desired, to form a use composition for injection into the pipeline. Suitably, the inhibitor composition-to-dilution liquid ratio is about 0.5:1 to 5:1.

Generally, the polymer solution used in the composition of the invention is present in an amount of about 30 to 70%, preferably 45 to 55%, by weight in admixture with the polymerization solvent. The polymer inhibition concentration in the pipeline, i.e. in the aqueous phase (water being inherently present therein) is about 0.1 to 3%, preferably 0.5-1%, by weight. The solvent* inhibition concentration, accordingly, is about 1 to 9% by weight of the aqueous phase.

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* total of all solvents present in the composition

PREPARATION OF INHIBITOR COMPOSITIONS

Example 1 illustrates the preparation of a 40 weight % solution of a copolymer of 97% by weight vinyl caprolactam and 3% by weight of 4-vinyl pyridine in 2-butoxy-ethanol (BGE).

EXAMPLE 1

Preparation of Vinyl Caprolactam (VCL)/4-Vinylpyridine (4-Vpy) (97/3) Copolymer in 2-Butoxyethanol

300.00 g of 2-butoxyethanol (BGE) was charged into a 1-l, 4-necked resin kettle, fitted with a reflux condenser, a nitrogen inlet tube, a propeller agitator, a thermal watch/thermocouple and a heating mantle. Nitrogen sparging was started and continued throughout the experiment. The kettle was then heated to 150°C and maintained at 150 $\pm$ 2°C throughout the experiment while keeping agitation speed at 250 rpm. A premix of 194.0 g of vinyl caprolactam, 6.0 g of 4-vinylpyridine and 4.0 g of di-t-butyl peroxide initiator (98.5% active) was prepared and pumped into the resin kettle over a period of 2 hours. After the completion of monomer feeding, the reaction mixture was held at 150°C for 60 minutes. Thereafter, 0.5 g of di-t-butyl peroxide was added hourly, five times, to react out residual monomers. The reaction was then held at 150°C for an additional 2 hours before cooling to ambient conditions. Vinyl caprolactam/4-vinylpyridine (87/3) copolymer thus obtained was 40% solids solution in 2-butoxyethanol (BGE). Gas chromatography (GC) analysis indicates that residual vinyl caprolactam and 4-vinylpyridine in the polymer are 0.86 and 0.05%, respectively. The polymer has a relative viscosity of 1.061 (1% in BGE, GPC weight-average molecular weight of 1,060, polyethylene glycol as standard).

Example 2 is representative of the effectiveness of the copolymer of the invention in corrosion inhibition of metals in natural gas pipelines.

EXAMPLE 2

The copolymer of Example 1 is diluted with monoethylene glycol and is used in gas hydrate inhibition in natural gas wells, whereupon dual functionality of gas hydrate inhibition and corrosion inhibition is demonstrated by its effectiveness in preventing corrosion in the pipeline.

GAS HYDRATE INHIBITION TESTING

Example 3 illustrates the effectiveness of the compositions of the invention to inhibit gas hydrate formation in a hydrocarbon fluid.

EXAMPLE 3

The composition of Example 1 prepared at 40 wt. % copolymer in BGE was tested under the experimental conditions of [MEG] = 5.4 wt%; [BGE] = 1.5 wt%; [P(VCAP/4VP)] = 1.0 wt%; fluid phase composition: saline water/gas condensate ratio = 1:1 vol/vol, and [NaCl] = 1.0 wt %; and at P = 85 bar, T = 4°C, which corresponds to 11.5°C of operating subcooling.

In this experiment, there were 3 passes out of 6 runs (i.e. no hydrate formation for >47 hours) with one failure after 18 hours, evidenced by a small pressure drop (1-2 bars) and no exotherm, thus indicating high inhibition efficiency of the tested formulation at the above sub-cooling**. The times for the onset of gas hydrate formation ($t-t_o$ min) were as follows:

>3969 min [5]*

>3969 min [6]

3258 min [4]

1089 min [4]

773 min [3]**

485 min [3]**

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* brackets indicate a given rig number

** Since only one-half inner volume of the autoclave is covered with the fluid phase containing inhibitor solution, the few short induction times observed are abnormal results representing onset of hydrate formation initiated at the metallic parts of the autoclave not contacting the inhibitor solution via water condensation from the vapor phase.

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. Accordingly, it is intended to be bound only by the following claims, in which:

CLAIMS:

1. A composition for preventing or retarding the formation of a gas hydrate or for reducing the tendency of a gas hydrate to agglomerate during the transport of a fluid comprising water and a hydrocarbon, through a conduit, comprising a copolymer of (a) vinyl caprolactam and (b) vinyl pyridine.

2. A composition according to claim 1, wherein (b) is quaternized.

3. A composition according to claim 2, wherein (b) is quaternized with a C_1-C_{18} alkyl halide.

4. A composition according to any one of claims 1 to 3, wherein the polymer further is a terpolymer with (c) vinyl pyrrolidone.

5. A composition according to claim 4, wherein, by weight, (a) is 70-97%; (b) is 3-25%; and (c) is up to 15%.

6. A composition according to any one of claims 1 to 5, wherein (b) is a 2- or 4-vinyl pyridine.

7. A single phase composition according to any one of claims 1 to 6, which is polymerized in butoxyethanol and includes monoethylene glycol as carrier solvent.

8. A composition according to any one of claims 1 to 7, wherein (a) has a molecular weight of about 500 to 2500.

9. A composition according to any one of claims 1 to 8, which has a cloud point > 10°C.

10. A single phase composition for preventing or retarding the formation of a gas hydrate or for reducing the

tendency of a gas hydrate to agglomerate, during the transport of a fluid comprising water and a hydrocarbon, through a conduit, where an aqueous phase is inherently present, comprising (a) a solution of a copolymer of vinyl caprolactam and a vinyl pyridine having a molecular weight in the range of about 500 to 2500, GPC, polyethylene glycol standard, made in (b) a polymerization solvent which is a glycol ether containing an alkoxy group having at least 3 carbon atoms, and including (c) a carrier solvent.

11. A composition according to claim 10, wherein the copolymer is a terpolymer with vinyl pyrrolidone.

12. A composition according to claim 10 or 11, further comprising (d) water, methanol or a mixture thereof.

13. A composition according to any one of claims 1 to 12, wherein the concentration of said composition is 0.3-1 wt.% in the conduit.

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