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(54) Title: DIUREA COMPOUND BASED THICKENERS FOR LIQUID AND SUPERCRITICAL HYDROCARBONS

(57) Abstract: The present invention relates to a composition comprising at least one compound of general formula (I) and at least one liquid or supercritical C₂-C₅ hydrocarbon. The present invention further relates to the use of the at least one compound of general formula (I) as thickener for the at least one liquid C₂-C₅ hydrocarbon. The invention also relates to a method of fracturing a subterranean formation penetrated by a wellbore with the composition of the present invention. The invention further relates to a method of enhanced oil recovery using the composition of the present invention.



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Diurea compound based thickeners for liquid and supercritical hydrocarbons

Field of the Invention

- 5 The present invention relates to a composition comprising at least one compound of general formula (I) and at least one liquid or supercritical C₂-C₅ hydrocarbon. The present invention further relates to the use of the at least one compound of general formula (I) as thickener for the at least one liquid C₂-C₅ hydrocarbon. The invention also relates to a method of fracturing a subterranean formation penetrated by a wellbore with the composition of the present in-
10 vention. The invention further relates to a method of enhanced oil recovery using the composition of the present invention.

Background of the Invention

- 15 Hydraulic fracturing is a widely used oil and gas production stimulation technique. It is a well-known process used to recover hydrocarbon fluids such as gases (e.g., natural gas) or liquids (e.g., oil or petroleum) that are otherwise trapped or present in the pores of underground formations. At its most basic level, hydraulic fracturing involves the creation of fractures (e.g., cracks, fissures, etc.) in rocks or underground formations which will allow hydrocarbon fluids
20 to flow toward a production well. Hydraulic fracturing of subterranean formations (also referred to as fracking), provides a pathway for hydrocarbon fluids to move more easily through tight low permeability (micro Darcy) formations (e.g., shale, certain clay sandstones, lime-stones, etc.) to a production well.
- 25 Fracturing fluids are designed to enable the initiation or extension of fractures and the simultaneous transport of suspended proppant (for example, naturally-occurring sand grains, resin-coated sand, sintered bauxite, glass beads, ultra-lightweight polymer beads and the like) into the fracture to keep the fracture open when the pressure is released.
- 30 Water based fracturing (hydrofracturing) is the most common one, in which the fracturing fluid comprising at least water, water-soluble thickeners and proppants are used. Although widely distributed, said technology has some drawbacks: when releasing the pressure after fracturing, a huge amount of water is returned to the surface through the injection well. Said wastewater produced from the formation typically is a mixture of used fracturing fluid and
35 formation water. Formation water usually comprises a very high amount of salts. Consequently, the wastewater produced also comprises salts and furthermore chemicals of the fracturing fluid or decompositions products thereof. Disposal of such a wastewater mixture may be expensive. Furthermore, by using water, the surfaces of the subterranean formation become wetted which may impair the production of crude oil from the formation. Intensified concerns
40 by the public regarding water pollution (requires ~3-6 million gallons of water per well) for hydrofracturing have prompted many companies to search for alternatives to hydrofracturing, especially in water-sensitive formations.

Petroleum fluids have been used for fracturing purpose since 1950. Because of its volatility, liquified petroleum gas (LPG) leaves no residue behind. The benefits of using high pressure volatile light alkanes for fracturing include the elimination of the formation damage associated with conventional aqueous fluids, and the ease of removal of the hydrocarbons via depressur-
5 ization, the absence of waste water, and the ability to recapture the alkanes at the wellhead after the proppant is placed. Liquid hydrocarbons (mixtures of propane, butane) and natural gas liquid (unfractionated hydrocarbon mixture comprising ethane, propane, butane, isobu-
tane, and pentane plus) have been used as fracturing fluids for waterless fracking. However, the disadvantage of these liquified alkane based fracturing fluids is the low viscosity. This re-
10 quires the use of certain gelling chemicals for the “gelation” or “thickening” of the light liquid alkanes to enable them to generate larger fractures and to carry higher concentrations of larger sand proppant particles.

US 3,368,627 describes a fracturing method that uses a combination of a liquid C₂-C₆ hydro-
15 carbon and CO₂ mix as the fracturing fluid.

US 9187996 B1 discloses a fracturing fluid mixture which is used to hydraulically fracture un-
derground formations in a reservoir, by mixing at least natural gas comprising methane and a
base fluid comprising an aqueous or hydrocarbon well servicing fluid to form the fracturing
20 fluid mixture, and injecting the fracturing fluid mixture into a well.

For oil formations, in order to obtain the desired fracture width, higher viscosity fracturing
fluids are employed. Consequently, higher loading of proppants is used to suitably prop open
the relatively wide fractures. Fluids with low viscosity typically lack sufficient viscosity to carry
25 such amounts of proppants, especially at high temperatures. A variety of chemicals/molecules
are used to increase the viscosity of the fracturing fluid. With any viscosity increase, some type
of gelling chemical (thickener) must be used first. Viscosity is used to carry proppant into the
formation, but when a well is being flowed back or produced, it is undesirable to have the
fluid pull the proppant out of the formation. For this reason, a chemical known as a breaker is
30 almost always pumped with all gel or crosslinked fluids to reduce the viscosity. This chemical is
usually an oxidizer or an enzyme. The oxidizer reacts with the gel to break it down, reducing
the fluid's viscosity and ensuring that no proppant is pulled from the formation. An enzyme
acts as a catalyst for the breaking down of the gel. Sometimes pH modifiers are used to break
down the crosslink at the end of a hydraulic fracture job, since many require a pH buffer sys-
35 tem to stay viscous. The rate of viscosity increase for several gelling agents is pH-dependent,
so that occasionally pH modifiers must be added to ensure viscosity of the gel.

Typical gelling chemicals include: (1) Conventional linear gels - These gels are cellulose deriva-
tives (carboxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl hydroxyethyl cellulose,
40 hydroxypropyl cellulose, methyl hydroxyl ethyl cellulose), guar or its derivatives (hydroxypro-
pyl guar, carboxymethyl hydroxypropyl guar), (2) Borate-crosslinked gels - These are guar-
based fluids cross-linked with boron ions (from aqueous borax/boric acid solution). These gels
have higher viscosity at pH 9 onwards and are used to carry proppants. After the fracturing

job, the pH is reduced to 3-4 so that the cross-links are broken and the gel is less viscous and can be pumped out. Organometallic-crosslinked fluids zirconium, chromium, antimony, titanium salts are known to crosslink the guar based gels. The crosslinking mechanism is not reversible. So once the proppant is pumped down along with the cross-linked gel, the fracturing part is done. The gels are broken down with appropriate breakers; (3) Aluminum phosphate-ester oil gels - Aluminum phosphate and ester oils are slurried to form cross-linked gel. These are one of the first known gelling systems.

WO 2007/098606 A1 discloses a fracturing system for a well, in which a mixture of propane and butane is injected into the well along with an inert gas such as nitrogen. The mixture of propane and butane is thickened with a gelling agent created by reacting diphosphorus pentoxide with triethyl phosphate and C₃-C₇ alcohol which is further reacted with aluminum sulfate.

US 2011/0284230 A1 discloses waterless fracturing method in which liquified petroleum gas (LPG) is used as a fracturing fluid. A gelling agent created by reacting diphosphorus pentoxide with triethyl phosphate and C₃-C₇ alcohol which is further reacted with aluminum sulfate.

WO2014036498 A2 relates to multi-arm star macromolecules which are used as thickening agents or rheology modifiers, for use in hydraulic fracturing fluid compositions.

WO 2016/064645 A1 describes a Y-Grade Natural gas liquid (NGL) stimulation fluid, comprising about 30% to 80% of ethane; about 15% to 50% of propane; about 15% to 45% of butane; about 15% to 40% of isobutane; about 5% to 25% of pentane plus, proppant, carbon dioxide, nitrogen and a gelling agent which includes at least one of phosphate esters and organometallic complex cross-linkers.

Aluminum phosphate-ester oil gels are very limited in use currently, because of formation damage and difficulty in cleanup. Due to the costs associated with guar, it is not economical to obtain the desired high viscosity by simply increasing the concentration of the guar polymer. Overly concentrated guar fracturing fluids lead to adverse effects for the formation and proppant pack, i.e., formation or proppant pack damage, offsetting the benefit brought by the fracturing process.

Use of the gelling agent based on guar gums, borate-crosslinked gels or aluminum phosphate-ester oil gels requires a gel breaker which is added to break the gel, after the fracturing.

In addition to the disadvantages of using the gelling agents as described above, their solubility in liquid hydrocarbon is another challenge, this being the reason that very few gelling agents are reported for the liquid hydrocarbons.

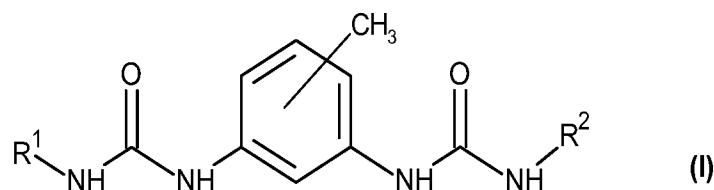
Additionally, gelling agents/thickeners are also employed in enhanced oil recovery(EOR) or tertiary recovery process. In the domestic oil production, enhanced oil recovery is used for recovering the residual oil trapped in the formation. For this, the known techniques are high pressure carbon dioxide flooding and flooding with natural gas liquids (NGL), which is primarily a mixture of ethane, propane, butane and a small amount of pentanes and higher alkanes. High pressure carbon dioxide or NGL has the ability to mix with oil to swell it, make it less viscous, detach it from the rock surface and cause the oil to flow more freely within the reservoir towards the production well. NGL flooding is more efficient than CO₂ flooding because the amount of oil recovered per amount of solvent injected is more. However, NGL has low density and viscosity relative to crude oil and thus it tends to exhibit gravity override as it flows through the formation, reducing oil recovery in the lower portions of reservoir. The NGL flow can be tailored by adding thickeners/gelling agents. Thickeners/gelling agents for ethane, propane, butane and pentane are intended to dissolve completely in these high-pressure fluid, forming a transparent, thermodynamically stable, single-phase solution capable of flowing through the porous media in a controlled manner. However, the thickeners/gelling agents being used for the thickening of the NGL for EOR are similar to those as described above for the waterless fracking, hence they exhibit the same drawbacks as indicated above. Accordingly, it is an object of the presently claimed invention to provide a gelling agent (thickener) which overcomes the problems associated with the gelling agents of the prior art. It is also an object to provide a gelling agent which is soluble in liquid hydrocarbons and supercritical hydrocarbons and whose viscosity can be easily lowered, without use of additional oxidative molecules or additional operations, after fracturing or recovery of oil is done.

Summary of the Invention

Surprisingly it was found that certain diurea compounds show improved thickening properties of liquid or supercritical hydrocarbons and lead to fracturing fluids with the desired viscosity. The diurea compounds of the present invention do not require a breaker molecule or an oxidizer to decrease the viscosity after the fracturing or after the recovery of oil.

Thus, in an aspect the presently claimed invention relates to a composition comprising

- (i) at least one liquid or supercritical C₂-C₅ hydrocarbon;
- (ii) at least one compound of general formula (I)

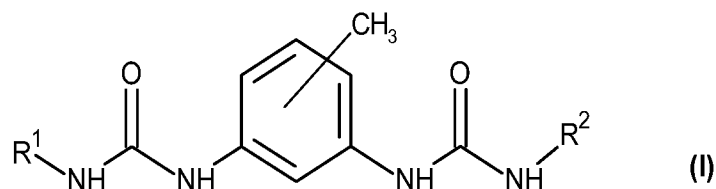


wherein

R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted C_1 - C_{14} alkyl.

In another aspect, the presently claimed invention relates to the use of the at least one compound of general formula (I) as thickener for the at least one liquid or supercritical C_2 - C_5 hydrocarbon.

In another aspect, the presently claimed invention relates to the use of the at least one compound of general formula (I)

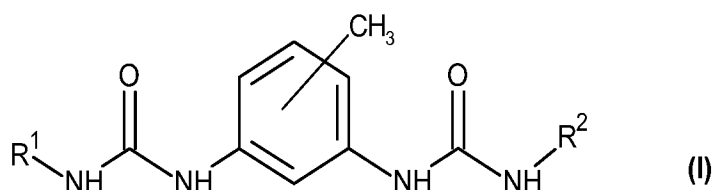


wherein

R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted C_1 - C_{14} alkyl;
as thickener for the at least one liquid or supercritical C_2 - C_5 hydrocarbon.

In another aspect, the presently claimed invention relates to the use of the composition comprising

- (i) at least one liquid or supercritical C_2 - C_5 hydrocarbon;
- (ii) at least one compound of general formula (I)

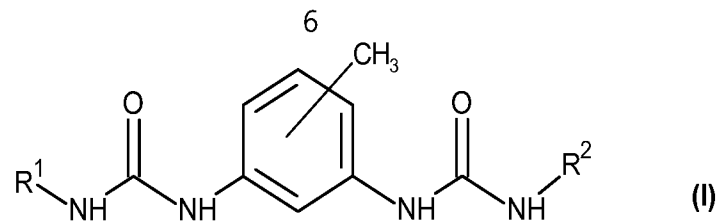


wherein

R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted C_1 - C_{14} alkyl;
for fracturing.

In another aspect, the present invention is directed to use of the composition comprising

- (i) at least one liquid or supercritical C_2 - C_5 hydrocarbon; and
- (ii) at least one compound of general formula (I)



wherein

R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted C_1 - C_{14} alkyl.

for enhanced oil recovery (EOR).

In another aspect, the present invention relates to a method of fracturing a subterranean formation penetrated by a wellbore, comprising the steps of

- (a) formulating the composition comprising the at least one liquid or supercritical C_2 - C_5 hydrocarbon, and at least one compound of general formula (I) with the at least one proppant to obtain a fracturing fluid, and
- (b) pumping the fracturing fluid of step (a) down the wellbore.

Detailed description of the Invention

Before the present compositions and formulations of the invention are described, it is to be understood that this invention is not limited to particular compositions and formulations described, since such compositions and formulation may, of course, vary. It is also to be understood that the terminology used herein is not intended to be limiting, since the scope of the present invention will be limited only by the appended claims.

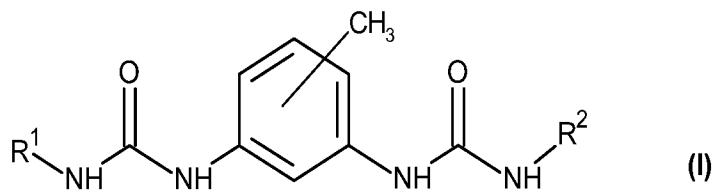
If hereinafter a group is defined to comprise at least a certain number of embodiments, this is meant to also encompass a group which preferably consists of these embodiments only. Furthermore, the terms "first", "second", "third" or "(a)", "(b)", "(c)", "(d)" etc. and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein. In case the terms "first", "second", "third" or "(A)", "(B)" and "(C)" or "(a)", "(b)", "(c)", "(d)", "i", "ii" etc. relate to steps of a method or use or assay there is no time or time interval coherence between the steps, that is, the steps may be carried out simultaneously or there may be time intervals of seconds, minutes, hours, days, weeks, months or even years between such steps, unless otherwise indicated in the application as set forth herein above or below.

In the following passages, different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment, but may. Furthermore, the particular features, structures or characteristics may be combined in any suitable manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments. Furthermore, while some embodiments described herein include some but not other features included in other embodiments, combinations of features of different embodiments are meant to be within the scope of the invention, and form different embodiments, as would be understood by those in the art. For example, in the appended claims, any of the claimed embodiments can be used in any combination.

In one aspect, the presently claimed invention relates to a composition comprising

- (i) at least one liquid or supercritical C₂-C₅ hydrocarbon;
- (ii) at least one compound of general formula (I)



wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁-C₁₄ alkyl.

- (i) Liquid or supercritical hydrocarbon

In an embodiment, the hydrocarbon is at least one liquid or supercritical C₂-C₅ hydrocarbon.

The at least one liquid or supercritical C₂-C₅ hydrocarbon is selected from the group consisting of ethane, n-propane, n-butane, n-pentane, isopropane, isobutane, isopentane, isomers and mixtures thereof.

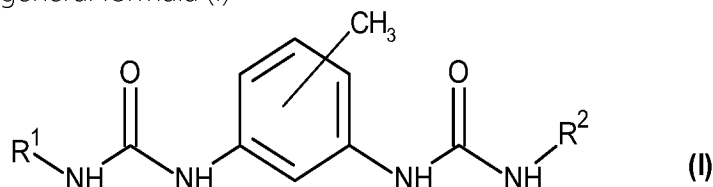
The at least one liquid or supercritical C₂-C₅ hydrocarbon is selected from the group consisting of n-propane, n-butane, n-pentane and mixtures thereof. The term 'liquid' refers to the C₂-C₅ hydrocarbon in a liquid state. C₂-C₅ hydrocarbon such as ethane, n-propane, isobutane are present in gas phase at ambient conditions and suitable pressure and temperature for liquefying them is well known to the person skilled in the art and the present invention is not limited by the choice of the same. However, hydrocarbon such as n-propane and isopropane exist as liquid at ambient conditions.

In an embodiment, the at least one liquified C₂-C₅ hydrocarbon (i) can be such as, but not limited to, a liquified petroleum gas (LPG) or a natural gas liquid (NGL). As is known to the person skilled in the art, LPG is a mixture of propane and butane, while NGL is a mixture of ethane, propane, butane and pentane. LPG is liquid under low pressure of 5-10 atmospheres but without the need to cool it. NGL is separated from the gas state in the form of liquids, in a field facility or in a gas processing plant through absorption or condensation.

A supercritical fluid is defined as any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. The term 'supercritical C₂-C₅ hydrocarbon' refers to C₂-C₅ hydrocarbon at a temperature and pressure above their respective critical point, where distinct liquid and gas phases do not exist. For instance, for supercritical propane, critical pressure = 42.5 bar and critical temperature = 97°C.

(ii) Compound of general formula (I)

In a preferred embodiment, the composition of the present invention comprises the at least one compound of general formula (I)



wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁-C₁₄ alkyl.

In connection with "alkyl", the term "substituted" within the scope of this invention is understood as meaning the substitution of hydrogen by 1, 2, 3, 4 or 5 substituents selected from the group consisting of F, Cl, Br, I, CN, NH₂, NH-C₁₋₆-alkyl, NH-C₁₋₆-alkylene-OH, N(C₁₋₆-alkyl)₂, N(C₁₋₆-alkylene-OH)₂, NO₂, SH, S-C₁₋₆-alkyl, S-benzyl, O-C₁₋₆-alkyl, O-C₁₋₆-alkylene-OH, =O, O-benzyl, C(=O)C₁₋₆-alkyl, CO₂H, C(=O)-O-C₁₋₆-alkyl, phenyl and benzyl. The substitution of hydrogen occurs either on different atoms or on the same atom, for example trisubstituted on the same carbon atom, as in the case of CF₃ or CH₂CF₃, or at different positions, as in the case

of $\text{CH}(\text{Cl})-\text{CH}=\text{CH}-\text{CHCl}_2$. Polysubstitution can be carried out with the same or with different substituents, such as, for example, in the case of $\text{CH}(\text{OH})-\text{CH}=\text{CH}-\text{CHCl}_2$.

Preferably, the substituents are selected from the group consisting of F, Cl, I, $\text{N}(\text{C}_{1-6}\text{-alkyl})_2$, $\text{N}(\text{C}_{1-6}\text{-alkylene-OH})_2$, NO_2 , S- $\text{C}_{1-6}\text{-alkyl}$, S-benzyl, O- $\text{C}_{1-6}\text{-alkyl}$, O- $\text{C}_{1-6}\text{-alkylene-OH}$, $=\text{O}$, O-benzyl, $\text{C}(=\text{O})\text{C}_{1-6}\text{-alkyl}$, CO_2H , $\text{C}(=\text{O})\text{-O-C}_{1-6}\text{-alkyl}$, phenyl and benzyl.

As used herein, “branched” denotes a chain of atoms with one or more side chains attached to it. Branching occurs by the replacement of a substituent, e.g., a hydrogen atom, with a covalently bonded aliphatic moiety.

Preferably, R^1 and R^2 are, independently of one another, selected from the group consisting of methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, 2-ethylhexyl, 1,5-dimethyl hexyl, isopropyl, isobutyl, isopentyl, 3-methyl-1-butyl, 2-methyl-1-butyl, 1-ethyl-1-propyl, 1-phenyl-1-ethyl, tert-butyl, isohexyl, isoheptyl, 2-propylheptyl, 1,1,3,3-tetramethyl-1-butyl, isononyl, isodecyl, isoundecyl, isododecyl, isotridecyl, isotetradecyl, and isomers thereof.

In a preferred embodiment, R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted $\text{C}_6\text{-C}_{13}$ alkyl.

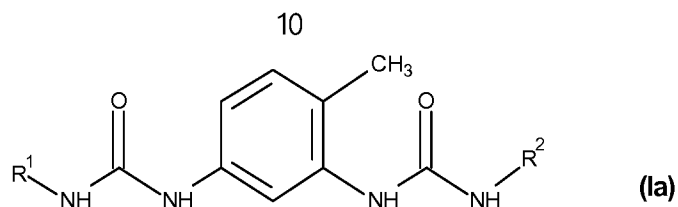
More preferably, R^1 and R^2 are, independently of one another, selected from the group consisting of n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, 2-ethylhexyl, 1,5-dimethyl hexyl, isopropyl, isobutyl, isopentyl, isohexyl, isoheptyl, 2-propylheptyl, 1,1,3,3-tetramethyl-1-butyl, isononyl, isodecyl, isoundecyl, isododecyl, isotridecyl and isomers thereof.

Most preferably, R^1 and R^2 are, independently of one another, selected from the group consisting of 2-ethylhexyl, 1,5-dimethyl hexyl, isotridecyl and isomers thereof.

The at least one compound of general formula (I) can be obtained by reacting diisocyanates with monoamines.

For the present invention, the diisocyanate is toluene diisocyanate (TDI). Toluene diisocyanate exists in 6 isomeric forms, of which toluene 2,4-diisocyanate and toluene 2,6-diisocyanate are commercially available. For the present invention, the preferred diisocyanates are toluene 2,6-diisocyanate (CAS 91-08-7) and toluene 2,4-diisocyanate (CAS 584-84-9) or mixtures thereof. A preferred diisocyanate is a mixture of the 2,4 and 2,6 isomers of toluene diisocyanate, preferably the mixture comprises 2,4 toluene diisocyanate in the range of $\geq 80\%$ to $\leq 98\%$, more preferably in the range of $\geq 80\%$ to $\leq 95\%$.

When toluene 2,4-diisocyanate is used as a diisocyanate, the at least one compound of general formula (Ia)

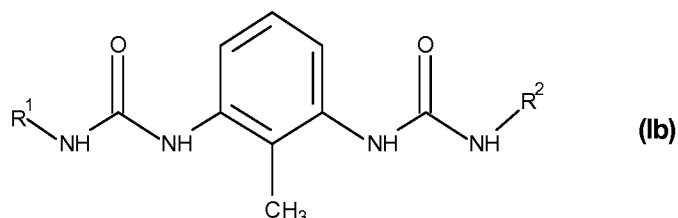


wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁-C₁₄ alkyl;

5 is obtained.

When toluene 2,6-diisocyanate is used as a diisocyanate, compounds of general formula (1b)



wherein

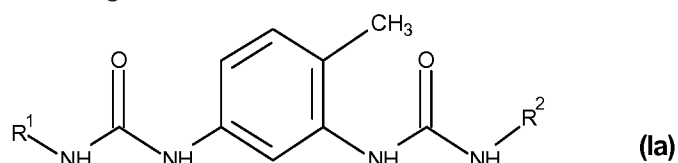
10 R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁-C₁₄ alkyl;

is obtained.

15 In case a mixture of diisocyanate, toluene 2,4-diisocyanate and toluene 2,6-diisocyanate is used, a mixture of compounds of general formula (1a) and compounds of general formula (1b) is obtained.

Accordingly, in a preferred embodiment, the composition comprises

- 20 (i) at least one liquid or supercritical C₂-C₅ hydrocarbon, and
 (ii) at least one compound of general formula (1a)



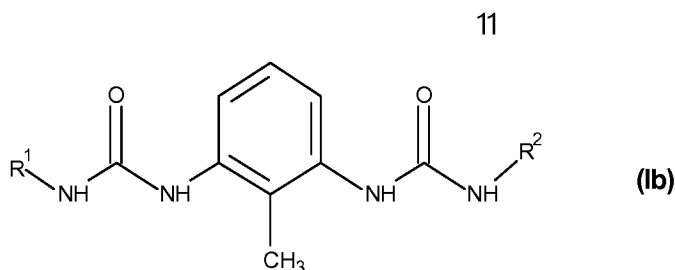
wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁-C₁₄ alkyl.

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In another preferred embodiment, the presently claimed invention is directed to the composition comprising

- (i) at least one liquid or supercritical C₂-C₅ hydrocarbon;
 (ii) at least one compound of general formula (1b)



wherein

R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted C_1 - C_{14} alkyl.

5

Preferably, the compounds of general formula (I) are prepared by reacting a mixture of toluene 2,4-diisocyanate and toluene 2,6-diisocyanate with a monoamine.

10 The monoamine is selected from the group consisting of methylamine, ethylamine, n-propylamine, n-butylamine, n-pentylamine, n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, n-undecylamine, n-dodecylamine, n-tridecylamine, n-tetradecylamine, 2-ethylhexylamine, 1,5-dimethyl hexylamine, isopropylamine, isobutylamine, isopentylamine, 3-methyl-1-butylamine, 2-methyl-1-butylamine, 1-Ethyl-1-propylamine, 1-phenyl-1-ethylamine, tert-butylamine, isohexylamine, isoheptylamine, 2-propylheptylamine, ,
15 1,1,3,3-tetramethyl-1-butylamine, isononylamine, isodecylamine, isoundecylamine, isododecylamine, isotridecylamine, isotetradecylamine, and isomers thereof.

In a preferred embodiment, the monoamine is selected from the group consisting of n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, n-undecylamine, n-dodecylamine, 2-ethylhexylamine, 1,5-dimethyl hexylamine, isopropylamine, isobutylamine, isopentylamine, isohexylamine, isoheptylamine, 2-propylheptylamine, 1,1,3,3-tetramethyl-1-butylamine, isononylamine, isodecylamine, isoundecylamine, isododecylamine, isotridecylamine and isomers thereof.

25 In a more preferred embodiment, the monoamine is selected from the group consisting of 2-ethylhexylamine, 1,5-dimethyl hexylamine, isotridecylamine and isomers thereof.

The monoamines are reacted with the diisocyanates in an organic solvent (F. Lortie, Langmuir 2002, 18, 7218). The resulting product is separated from the organic solvent and then dissolved in liquid or supercritical hydrocarbon to prepare inventive compositions.

30 In a preferred embodiment, the at least one compound of general formula (I) has molecular weight in the range of ≥ 200 g/mol to ≤ 2000 g/mol, more preferably in the range of ≥ 200 g/mol to ≤ 1500 g/mol, even more preferably in the range of ≥ 200 g/mol to ≤ 1400 g/mol or ≥ 300 g/mol to ≤ 1400 g/mol and most preferably in the range of ≥ 400 g/mol to ≤ 1400 g/mol.

In another embodiment, the presently claimed invention is directed to a composition comprising the at least one compound of general formula (I) in an amount in the range of ≥ 0.01 to ≤ 10.0 % by weight of the final weight of the composition, more preferably in the range of ≥ 0.01 to ≤ 10.0 % by weight or ≥ 0.01 to ≤ 9.0 % by weight or ≥ 0.01 to ≤ 8.0 % by weight or ≥ 0.01 to ≤ 7.0 % by weight or ≥ 0.01 to ≤ 6.0 % by weight or ≥ 0.01 to ≤ 5.0 % by weight, ≥ 0.01 to ≤ 4.0 % by weight or ≥ 0.01 to ≤ 3.0 % by weight or ≥ 0.01 to ≤ 2.0 % by weight or even more preferably in the range of ≥ 0.05 to ≤ 10.0 % by weight or ≥ 0.05 to ≤ 9.0 % by weight or ≥ 0.05 to ≤ 8.0 % by weight or ≥ 0.05 to ≤ 7.0 % by weight or ≥ 0.05 to ≤ 6.0 % by weight or ≥ 0.05 to ≤ 5.0 % by weight or ≥ 0.05 to ≤ 4.0 % by weight or ≥ 0.05 to ≤ 3.0 % by weight or ≥ 0.05 to ≤ 2.0 % by weight and most preferably in the range of ≥ 0.01 to ≤ 10.0 % by weight or ≥ 0.01 to ≤ 9.0 % by weight or ≥ 0.01 to ≤ 8.0 % by weight or ≥ 0.01 to ≤ 7.0 % by weight or ≥ 0.01 to ≤ 6.0 % by weight or ≥ 0.01 to ≤ 5.0 % by weight or ≥ 0.01 to ≤ 4.0 % by weight or ≥ 0.01 to ≤ 3.0 % by weight or ≥ 0.01 to ≤ 2.0 % by weight; in each case by weight of the final weight of the composition.

The at least one compound of general formula (I) may be solid or sticky, wax-like compound at ambient conditions.

In an embodiment, the at least one compound of general formula (I) may be dissolved in a solvent in which they do not self-assemble, but rather are molecularly dissolved, prior to their addition to the liquid or supercritical hydrocarbons. This may result in concentrated solutions with low viscosities facilitating handling and mixing with the liquid or supercritical hydrocarbons which are to be thickened according to the invention.

In a preferred embodiment, the suitable solvents are C_1 - C_{30} alcohols. C_1 - C_{30} alcohols are selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, 2-ethylhexanol, 2-propylhepanol, isononanol, decanol, dodecanol. Suitable solvents may include (poly)alkylene glycols or alkyl (poly)alkylene glycols like polypropylene glycol, polyethylene glycol, polybutylene glycol, butylene glycol, propylene glycol, ethylene glycol, methyl propylene glycol, methyl dipropylene glycol, methyl tripropylene glycol, butyl propylene glycol, butyl dipropylene glycol, butyl tripropylene glycol, methyl ethylene glycol, methyl diethylene glycol, methyl triethylene glycol, butyl ethylene glycol, butyl diethylene glycol, butyl triethylene glycol. Further suitable solvents include water, tetrahydrofuran, 1,4-butanediol, 1,3-propylenglycol, and aromatic solvents like toluene, xylene, solvent naphtha, alkylated aromatics like Wibarcan[®]. The addition of chlorides may further decrease the viscosity of concentrated solution of the diurea compounds, for example NaCl, LiCl, KCl, NMe₄Cl and NBu₄Cl.

Proppants

The fracturing fluid further comprises at least one proppant which is suspended in the fracturing fluid. Proppants are small hard particles which remains in place in the fractures once the high pressure is removed, and thereby props open the fractures to enhance the flow of oil

into the wellbore. Consequently, the proppant increases the procurement of oil by creating a high-permeability, supported channel through which the oil can flow.

Suitable proppants are known to the skilled artisan. Examples of proppants include naturally-occurring proppants such as sand grains, nut shells, minerals, gravels, mine tailings, coal ashes, rocks, smelter slag, diatomaceous earth, crushed charcoal, micas, sawdust, wood chips, and synthetically produced proppants such as silica proppants, ceramic proppants, metallic proppants, synthetic organic proppants, and mixtures thereof. Proppant comprising a particle and a polycarbodiimide coating disposed on the particle as described in WO 2010/049467 A1 can also be used.

Resin coated versions of sand grains is also a suitable proppant.

Typical resin coatings include bisphenols, bisphenol homopolymers, blends of bisphenol homopolymers with phenol-aldehyde polymer, bisphenol-aldehyde resins and polymers, phenol-aldehyde polymers and homopolymers, modified and unmodified resoles, phenolic materials including arylphenols, alkylphenols, alkoxyphenols, and aryloxyphenols, resorcinol resins, epoxy resins, novolak polymer resins, novolak bisphenol-aldehyde polymers and waxes, as well as precured or curable versions of such resin coatings.

Silica proppants suitable for use, but are not limited to, glass spheres and glass microspheres, glass beads, silica quartz sand, and sands of all types such as white or brown sand. In case of silica fibers being used, the fibers can be straight, curved, crimped or spiral shaped, and can be of any grade, such as E-grade, S-grade and AR-grade. Examples of suitable resin-coated silica proppants are for example FlexSand™ LS, FlexSand™ M, available from BJ services, U.S., TX and Tempered HS®, Tempered LC®, Tempered DC® and Tempered TF® from Santrol, Fresno, TX.

Examples of suitable ceramic proppants suitable for use are ceramic beads, ultra-lightweight porous ceramics, economy lightweight ceramics such as 'Econoprop™, lightweight ceramics such as Carbolite®, intermediate strength ceramics such as Carboprop®, high strength ceramics such as Carbohsp®, sintered bauxite, encapsulated ceramic proppants as well as any resin coated or resin impregnated version of these.

Metallic proppants suitable for use include, but are not limited to, aluminium shot, aluminium pellets, aluminium needles, aluminium wire, iron shot, steel shot, and the like, as well as any resin coated versions of these metallic proppants.

Examples of synthetic organic proppants are plastic particles, plastic beads, nylon beads, nylon pellets, styrene divinyl benzene beads, carbon fibers such as Panex® carbon fibers from Zoltek Corporation, ultra-lightweight polymer beads and resin agglomerate particles as well as resin coated versions thereof.

In a preferred embodiment, the amount of proppant in the fracturing fluid is in the range of ≥ 50 kg to ≤ 3500 kg per m^3 of the fracturing fluid, preferably in the range of ≥ 50 kg to ≤ 1200 kg per m^3 of the fracturing fluid.

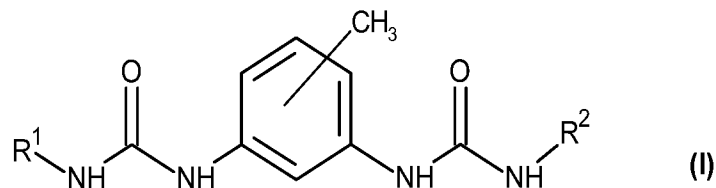
5 Additives

Depending upon the type of subterranean formation being treated and the intended type of treatment operation being conducted, other components may be optionally included in one or both of the proppant slurry and non-proppant injection liquid. A person having ordinary skill in the art, with the benefit of this disclosure, will recognize when such optional additives should be included, as well as the appropriate amounts to include.

Such components may include, for example, salts, pH control additives, surfactants, foaming agents, antifoaming agents, breakers, biocides, crosslinkers, additional fluid loss control agents, stabilizers, chelating agents, scale inhibitors, gases, mutual solvents, particulates, corrosion inhibitors, oxidizing agents, reducing agents, antioxidants, relative permeability modifiers, viscosifying agents, scale inhibitors, emulsifying agents, de-emulsifying agents, iron control agents, clay control agents, flocculants, scavengers, lubricants, friction reducers, viscosifiers, weighting agents, hydrate inhibitors, consolidating agents, delay agents, any combination thereof, and the like. Such components may include gelling/thickening agents reported in the state-of-the art such as tributyltin fluoride (TBTF), hydroxyl aluminum bis(2-ethylhexanoate) (HADEH), crosslinked phosphate ester (HGA70 C6 + HGA 65), silanol and ultra-high molecular weight poly- α -olefin drag reducer (DRA), gelling agent created by reacting diphosphorus pentoxide with triethyl phosphate and C_3 - C_7 alcohol which is further reacted with aluminium sulfate, cellulose and cellulose derivatives, multi-arm star macromolecules.

However, in a more preferred embodiment, the at least one compound of general formula (I) are by themselves efficient thickening agents for the at least one C_2 - C_5 liquid or supercritical hydrocarbon and do not require additional gelling/thickening agents as additives.

In an aspect, the present invention is directed to use of the at least one compound of general formula (I)

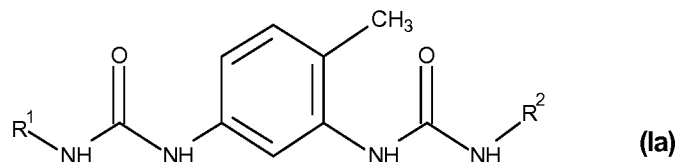


wherein

R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted C_1 - C_{14} alkyl;
as thickener for the at least one liquid or supercritical C_2 - C_5 hydrocarbon.

15

In another embodiment, the present invention is directed to use of the at least one compound of general formula (Ia)



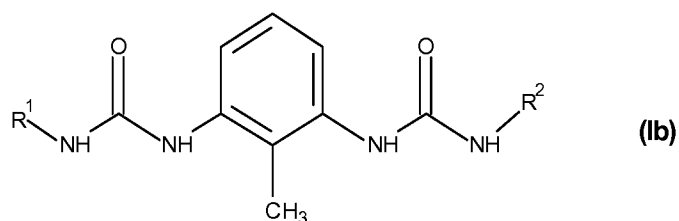
wherein

5

R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted C_1 - C_{14} alkyl;
as thickener for the at least one liquid or supercritical C_2 - C_5 hydrocarbon.

10

In an embodiment, the present invention is directed to use of the at least one compound of general formula (Ib)



wherein

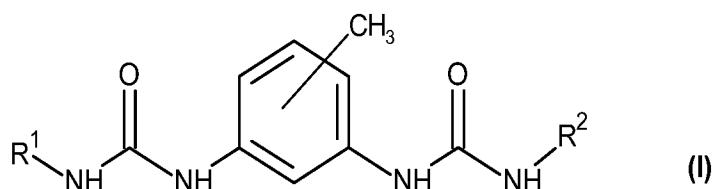
15

R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted C_1 - C_{14} alkyl;
as thickener for the at least one liquid or supercritical C_2 - C_5 hydrocarbon.

In another aspect, the present invention is directed to use of the composition comprising

20

- (i) at least one liquid or supercritical C_2 - C_5 hydrocarbon; and
- (ii) at least one compound of general formula (I)



wherein

25

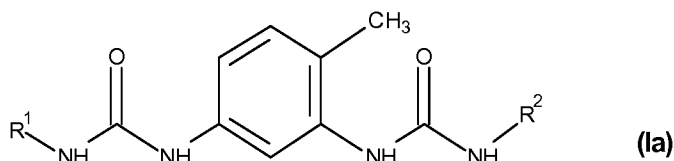
R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted C_1 - C_{14} alkyl.

for fracturing.

16

In another embodiment, the present invention is directed to use of the composition comprising

- (i) at least one liquid or supercritical C₂-C₅ hydrocarbon; and
- (ii) at least one compound of general formula (Ia)



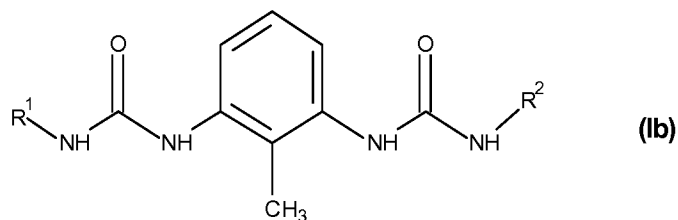
wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁-C₁₄ alkyl.

for fracturing.

In another embodiment, the present invention is directed to use of the composition comprising

- (i) at least one liquid or supercritical C₂-C₅ hydrocarbon; and
- (ii) at least one compound of general formula (Ib)



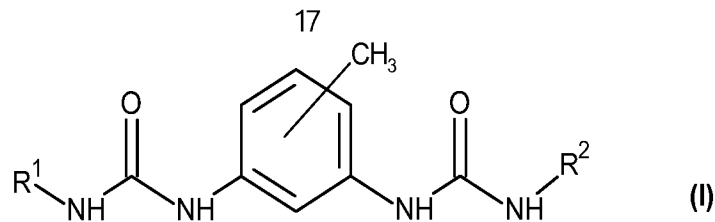
wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁-C₁₄ alkyl.

for fracturing.

In another aspect, the present invention is directed to use of the composition comprising

- (i) at least one liquid or supercritical C₂-C₅ hydrocarbon; and
- (ii) at least one compound of general formula (I)



wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted
 5 C₁-C₁₄ alkyl.

for enhanced oil recovery (EOR).

10 In another aspect, the present invention relates to a method for fracturing a subterranean formation.

In an embodiment, the method of fracturing a subterranean formation according to the present invention may be applied to any subterranean formation, preferably hydrocarbon containing subterranean formations. The hydrocarbons may be oil and/or gas. Besides oil and/or gas the formations may contain water which usually comprises salts. The salinity of the formation water may be in the range of $\geq 10,000$ ppm to $\leq 230,000$ ppm.
 15

The formations may be sandstone, carbonate or shale formations and the formation temperature may be up to 175°C.

In a preferred embodiment, inert gas such as nitrogen may be used as a gas blanket. When nitrogen is added to the fracturing fluid, the method has a particular utility for fracturing coal or shale formations.
 20

According to an embodiment, a foam may be created by the mixing of composition according to the present invention with inert gases such as nitrogen or carbon dioxide, where said nitrogen concentration is greater than 50% or where said carbon dioxide concentration is greater than 35%, or by a combination of nitrogen and carbon dioxide where said combined concentration of nitrogen and carbon dioxide is greater than 50% causes the resulting gaseous mixture to be outside the flammability limit.
 25

For applying the method according to the present invention to the formation, the formation is penetrated by at least one wellbore. The wellbore may be a "fresh" wellbore drilled into the formation which needs to become prepared for oil and/or gas production.

30 In another embodiment, the wellbore may be a production well which already has been used for producing oil and/or gas but the production rate decreased and it is necessary to fracture the formation (again) in order to increase production.

The method according to the present invention comprises at least two process steps (a) and (b). The method may optionally comprise further process steps.

In a preferred embodiment, the method of fracturing a subterranean formation penetrated by a wellbore, comprises the steps of

- 5 (a) formulating the composition comprising at least one liquid or supercritical C₂-C₅ hydro-
car
-bon and at least one compound of general formula (I) with the at
least one proppant to obtain a fracturing fluid, and
10 (b) pumping the fracturing fluid of step (a) down the wellbore.

10 In course of process step (a) a fracturing fluid comprising at least one liquid or supercritical C₂-C₅ hydrocarbon, at least one compound of general formula (I) and at least one proppant is formulated. The fracturing fluid may contain optionally further components/additives.

- 15 In an alternate process step (a), a fracturing fluid comprising at least one liquid C₂-C₅ hydro-
carbon, at least one compound of general formula (I), at least one proppant, an inert gas se-
lected from nitrogen and carbon dioxide or mixtures thereof and at least one emulsifying
agent is formulated.

- 20 In course of process step (b) the fracturing fluid is pumped into a wellbore. In a preferred em-
bodiment, the fracturing fluid is pumped in to the wellbore at a rate and pressure sufficient to
flow into the formation and to initiate or extend a fracture in the formation. In order to initiate
or to extend fractures in the formation, a bottom hole pressure sufficient to open a fracture in
the formation is necessary. The bottom hole pressure is determined by the surface pressure
25 produced by the surface pumping equipment and the hydrostatic pressure of the fluid col-
umn in the wellbore, less any pressure loss caused by friction. The minimum bottom hole
pressure required to initiate and/or to extend fractures is determined by formation properties
and therefore will vary from application to application. Methods and equipment for fracturing
procedures are known to the skilled artisan. The fluid simultaneously transports suspended
30 proppants and the proppant becomes deposited into the fractures and holds fractures open
after the pressure exerted on the fracturing fluid has been released.

- In course of further process steps, such as step (c), the applied pressure is reduced thereby
allowing at least a portion of the injected hydrocarbons to become recovered from the for-
35 mation. Upon reducing the applied pressure, the pressurized hydrocarbons stream, by virtue
of their own pressure, back to the surface. Reducing the pressure allows the fractures to close.
Proppant "props" fractures open and fracturing fluid is shut in or allowed to flow back. At the
surface, chokes may be used to generate a pressure differential to allow fluid to begin to flow
from the formation into the well bore.

40

Advantages compared to thickeners known in the state-of-the-art:

1. Diurea compounds of general formula (I) are more shear stable compared to high molecular weight polymers
2. The thickening efficiency of the diurea compounds of general formula (I) is higher than state-of-the-art thickeners for propane and butane.
- 5 3. No additional requirement of adding gel breakers or oxidizing molecules.

Examples:

Compounds

Toluene 2,4-diisocyanate (TDI) 95%,

5 1,5-Dimethylhexylamine 99%, are available from Aldrich.

2-Ethylhexylamine (2-EH NH_2) 99%,

Tridecylamine isomer mixture (iC₁₃H₂₇NH₂), CAS 86089-17-0.

10 Kerocom® PIBA (65% by weight solution of polyisobutylene amine based on high-reactivity polyisobutene, M_n=1000, in an aliphatic hydrocarbon mixture) are available from BASF SE, Ludwigshafen, Germany.

Heptadecylamine isomer mixture (iC₁₇H₃₅NH₂) was obtained by alcohol amination of heptadecanol M (isomer mixture of primary heptadecanols, branched and linear, CAS no. 90388-00-4, from BASF SE) as described in WO201101303.

n-Pentane, 98% from Aldrich

Propane, 99.99% from Matheson

20 TBTF: Tributyltin fluoride

HADEH: Hydroxyl aluminum bis(2-ethylhexanoate)

HGA70 C6 + HGA 65: Crosslinked phosphate ester by Lubrizol Oilfield Solutions

Silanol: Polydimethylsiloxane Silanol SE 30 (Mw 972540) from Momentive.

25 DRA: Ultra-high molecular weight poly- α -olefine drag reducer (Liquid-Power™ Flow Improver) from Lubrizol Specialty Products, M $\geq 2 \cdot 10^7$ g/mol.

Methods

Amine number

30 The total amine number (titration with perchloric acid) was determined according to DIN EN ISO 9702.

Preparation of diurea compounds of general formula (I)

35 Example 1 was prepared as described in F. Lortie et al., Langmuir 2002, 18, 7218-7222.

Example 4 was prepared as described in V. Simic et al., J. Am. Chem. Soc. 2003, 125, 13148-13154.

General procedure for the preparation of examples 2, 3, and 5:

40

A solution of the toluene 2,4-diisocyanate in dichloromethane (1.0 equivalent, 3.4 ml solvent/mmol diisocyanate) was admixed with a solution of the amine in dichloromethane (2.0 equivalents according to total amine number, 0.67 ml solvent/mmol amine) at room tempera-

ture. The exothermic reaction was cooled. After the addition was complete, stirring was continued at room temperature for 2 hours. The precipitated product was filtered and recrystallized from ethyl acetate.

5 Table 1

Example	Amine 1	Equivalents of amine 1	Amine 2	Equivalents of amine 2	Molecular weight of diurea compounds of general formula(I) (g/mol)
1	2-EH ₂ NH ₂	2.0	none	-	433
2	iC ₁₃ H ₂₇ NH ₂	2.0	none	-	572
3*	iC ₁₇ H ₃₅ NH ₂	2.0	none	-	685
4	1,5-Dimethyl hexyl amine	2.0	none	-	433
5*	iC ₁₃ H ₂₇ NH ₂	1.80	PIBA	0.20	739

* = not within the scope of the invention

10 Determination of the rheology-modifying properties in n-pentane

0.1 g of the compound under test was stirred in 99.9 g n-pentane at room temperature until complete dissolution. The rheological data were determined by using a low shear rheometer LS 300 from proRheo (Germany). The rheometer is designed to measure low viscous fluids. The geometry used was a concentric cylinder device of Couette type with rotating cup. The diameters of cup and bob are 6 mm and 5.5 mm, respectively. The bob is of DIN type (with conical end) and has a length of 8 mm. Evaporation of the volatile components was retarded by measuring at 20°C.

15 All viscosities have been measured as a function of the shear rate at a constant concentration of 0.1% (w/w). Significant shear thinning behavior was found for the samples 2 and 4. Nevertheless, even when the other samples show a less pronounced shear thinning, there is still an indication of a shear induced structural orientation with the shear thinning behavior in the viscosity regime of 1-2 mPas.

20 In order to better compare the viscosifying efficiency a relative viscosity value was calculated from the values at 5 s⁻¹ for samples 2 and 4. For the other samples the plateau value from the zero-shear viscosity plateau was taken. The relative viscosity is the ratio of the viscosity of the fluid with the dissolved thickener to the viscosity of the pure fluid.

The following results were obtained:

Table 2

Sample	Relative Viscosity
Example 1	473
Example 2	171
Example 3*	7.2

Example 4	545
Example 5*	3.8

* = not within the scope of the invention

The above Table 2 indicates that by adding the inventive compounds even in small quantities, a huge increase in the viscosity can be achieved.

5

Determination of solubility and cloud point pressures in propane:

The solubility of example 4 in propane was assessed using an invertible, variable volume cell as described in A. Dhuwe et al., Journal of Petroleum Science and Engineering, 145, 2016, 266 and A. Dhuwe et al., J. of Supercritical Fluids 2016, 114, 9. The samples required heating to 110-115°C and stirring at 5000 psi in propane to attain dissolution. Stable, transparent solutions were obtained at these conditions. The solutions were then cooled to the desired T and then slowly expanded to get the cloud point pressures, which are summarized in table 3.

15 Table 3

Entry	Concentration of compound of Ex. 4 in propane [wt%]	T [°C]	Cloud Point [psi]
1.	0.5	25	1279
2.	0.5	40	1685
3.	0.5	60	1922
4.	0.5	80	2604
5.	0.5	100	3443
6.	1.0	25	1312
7.	1.0	40	1721
8.	1.0	60	1950
9.	1.0	80	2662
10.	1.0	100	3580
11.	1.5	25	1512
12.	1.5	40	1830
13.	1.5	60	2130
14.	1.5	80	2814
15.	1.5	100	3804
16.	2.0	25	1612
17.	2.0	40	1948
18.	2.0	60	2346
19.	2.0	80	3068
20.	2.0	100	4060

The above Table indicates that the compound of inventive example 4 is quite soluble in propane. The resultant solution is transparent and stable above the cloud point pressure. Cloud

point pressures range between ~1000 – 4000 psi over the 0.5 – 2.0wt% of the compound of inventive example 4 and at temperature range of 25 °C-100 °C, with the highest cloud point pressure being associated with the highest concentration and temperature.

5 Determination of relative viscosities in propane

Falling ball viscometry was employed via measuring the terminal velocity of a close-clearance glass that falls through the solution after the cell is rapidly inverted as described in A. Dhuwe et al., Journal of Petroleum Science and Engineering, 145, 2016, 266 and A. Dhuwe et al., J. of Supercritical Fluids 2016, 114, 9. Relative viscosity (solution viscosity/viscosity of the pure propane) was obtained as a function of concentration, pressure and temperature. All measurements were taken at pressures greater than the cloud point pressure (i.e. in the single-phase region). In all cases the surface-average shear rate on the falling ball is about 7000/(relative viscosity) s⁻¹.

Table 4

Entry	Concentration of Ex. 4 in propane [wt%]	T [°C]	Pressure [psi]	Relative Viscosity
1.	0.5	40	5000	436
2.	0.5	40	7000	450
3.	0.5	40	8000	465
4.	0.5	40	9000	478
5.	0.5	60	5000	118
6.	0.5	60	7000	119
7.	0.5	60	8000	123
8.	0.5	60	9000	127
9.	0.5	80	5000	19.2
10.	0.5	80	7000	20.6
11.	0.5	80	8000	21.7
12.	0.5	80	9000	22.9
13.	0.5	100	5000	2.47
14.	0.5	100	7000	2.51
15.	0.5	100	8000	2.59
16.	0.5	100	9000	2.65
17.	1.0	80	5000	196
18.	1.0	80	7000	201
19.	1.0	80	8000	204
20.	1.0	80	9000	208
21.	1.0	100	5000	3.61
22.	1.0	100	7000	3.80

24

23.	1.0	100	8000	3.89
24.	1.0	100	9000	3.96
25.	1.5	80	5000	264
26.	1.5	80	7000	266
27.	1.5	80	8000	268
28.	1.5	80	9000	272
29.	1.5	100	5000	5.50
30.	1.5	100	7000	5.78
31.	1.5	100	8000	6.23
32.	1.5	100	9000	6.50
33.	2.0	80	5000	365
34.	2.0	80	7000	385
35.	2.0	80	8000	391
36.	2.0	80	9000	406
37.	2.0	100	5000	17.6
38.	2.0	100	7000	18.3
39.	2.0	100	8000	19.1
40.	2.0	100	9000	20.5

The ball was able to fall for compound of inventive example 4 at a concentration of 0.5 wt.%, 1.0 wt.%, 1.5 wt.% and 2.0wt% and temperature of 80 °C and 100 °C. The ball was not able to fall through the extremely viscous transparent solutions at 40 °C and 60 °C and concentrations of 1.0, 1.50 and 2.0 wt%. The ball was not able to fall through the extremely viscous transparent solutions at 25°C and concentrations of 0.50, 0.75, 1.00, 1.25, 1.50 and 2.00wt%.

The above table indicates that the compound of inventive example 4 is a remarkable thickener for propane. There is an increase of viscosity with higher concentrations and a decrease with increasing temperature. As the fracturing fluid goes down into the subterranean borewell, the temperature rises and with the rise in the temperature, the viscosity of the inventive compound of the present invention decreases, thereby obviating the need of any oxidizers which are usually employed for decreasing the viscosity of the polymers after the fracturing fluid has reached the desired region. Thus, the inventive compounds of the present invention are suitable thickening agents for the fracturing process. It is believed that the inventive compounds of general formula (I) form tube-like structures ("supramolecular polymers") via hydrogen-bonding as described for example 1 in liquid hydrocarbons like dodecane and toluene in V. Simic et al., J. Am. Chem Soc. 2003, 125, 13148.

Comparison of the rheology modifying properties with state-of-the-art thickeners

As comparative examples, the rheology-modifying properties of the state of the art thickeners, namely, tributyltin fluoride (TBTF), hydroxyl aluminum bis(2-ethylhexanoate) (HADEH),

crosslinked phosphate ester (HGA70 C6 + HGA 65), silanol and ultra-high molecular weight poly- α -olefin drag reducer (DRA) are summarized in table 5. The data was obtained from Aman Kishorji Dhuwe, Thickeners for Natural Gas Liquids to improve the Performance in Enhanced Oil Recovery and Dry Hydraulic Fracturing, M.S. Thesis, University of Pittsburgh, 2016

- 5 (available online: <http://d-scholarship.pitt.edu/26533/>). Parts of the thesis have been published in A. Dhuwe et al., Journal of Supercritical Fluids, 114, 2016, 9; A. Dhuwe et al., Journal of Petroleum Science and Engineering, 145, 2016, 266. The results from table 5 were obtained using the same procedure as the results for inventive example 4 in table 4.

10 Table 5

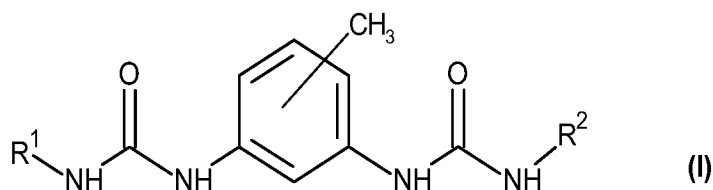
Compound	Concentration of compound in propane [wt%]	T [°C]	Pressure [psi]	Relative Viscosity
TBTF	0.5	40	6000	≤ 10
TBTF	0.5	40	8000	≤ 10
TBTF	0.5	40	9000	≤ 10
TBTF	0.5	60	6000	≤ 6
TBTF	0.5	60	8000	≤ 6
TBTF	0.5	60	9000	≤ 6
TBTF	1	100	8000	≤ 2
TBTF	1	100	9000	≤ 2
HADEH	0.5	60	6000	≤ 4
HADEH	0.5	60	8000	≤ 4
HADEH	0.5	60	9000	≤ 4
HADEH	0.5	40	6000	≤ 5
HADEH	0.5	40	8000	≤ 5
HADEH	0.5	40	9000	≤ 5
HADEH	1	80	6000	≤ 20
HADEH	1	80	8000	≤ 20
HADEH	1	80	9000	≤ 20
HGA70 C6 + HGA 65	0.5	60	7000	≤ 3
HGA70 C6 + HGA 65	0.5	60	7000	≤ 3
HGA70 C6 + HGA 65	0.5	60	9000	≤ 3
Silanol	2.0	25	7000	≤ 2
Silanol	2.0	25	8000	≤ 2
Silanol	2.0	25	8000	≤ 2
DRA	0.5	60	5000	≤ 10
DRA	0.5	60	6000	≤ 10
DRA	0.5	60	8000	≤ 10

The comparison shows that inventive compound of example 4 has a superior thickening efficiency for propane compared to the state-of-the-art thickeners. The thickening efficiency of the inventive compound of example 4 is more than ten times higher than those of the thickeners of the state-of-the-art.

Claims

1. A composition comprising

- (i) at least one liquid or supercritical C₂-C₅ hydrocarbon; and
 (ii) at least one compound of the general formula (I)

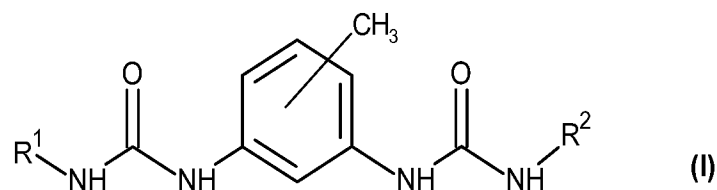


wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁-C₁₄ alkyl.

2. The composition according to claim 1, wherein the at least one liquid or supercritical C₂-C₅ hydrocarbon (i) is selected from the group consisting of ethane, n-propane, n-butane, n-pentane, isopropane, isobutane, isopentane, isomers and mixtures thereof.
3. The composition according to claim 1 or 2, wherein the at least one liquid or supercritical C₂-C₅ hydrocarbon (i) is selected from n-propane, n-butane, n-pentane, isomers and mixtures thereof.
4. The composition according to claim 1, wherein R¹ and R² are, independently of one another, selected from the group consisting of methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, 2-ethylhexyl, 1,5-dimethyl hexyl, isopropyl, isobutyl, isopentyl, 3-methyl-1-butyl, 2-methyl-1-butyl, 1-ethyl-1-propyl, 1-phenyl-1-ethyl, tert-butyl, isohexyl, isoheptyl, 2-propylheptyl, 1,1,3,3-tetramethyl-1-butyl, isononyl, isodecyl, isoundecyl, isododecyl, isotridecyl, isotetradecyl, and isomers thereof.
5. The composition according to claim 1, wherein R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₆-C₁₃ alkyl.
6. The composition according to claim 5, wherein R¹ and R² are, independently of one another, selected from the group consisting of n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, 2-ethylhexyl, 1,5-dimethyl hexyl, isopropyl, isobutyl, isopentyl, isohexyl, isoheptyl, 2-propylheptyl, 1,1,3,3-tetramethyl-1-butyl, isononyl, isodecyl, isoundecyl, isododecyl, and isomers thereof.

7. The composition according to one or more of claims 1 to 6, further comprising at least one proppant.
8. The composition according to claim 7, wherein the at least one proppant is selected from the group consisting of sand grains, resin-coated sand, sintered bauxite, glass beads, glass spheres, glass microspheres, silica quartz sand, ultra-lightweight polymer beads, minerals, ceramic beads, nut shells, gravels, mine tailings, coal ashes, rocks, smelter slag, diatomaceous earth, crushed charcoals, micas, sawdust, wood chips, resinous particles, polymeric particles, plastic particles, plastic beads, nylon pellets, styrene divinyl benzene beads, carbon fibers and combinations thereof.
9. The composition according to one or more of claims 1 to 8, further comprising at least one inert gas selected from nitrogen, carbon dioxide and mixtures thereof.
10. The composition according to one or more of claims 1 to 9, wherein the at least one compound of general formula (I) is present in an amount in the range of ≥ 0.01 wt.% to ≤ 5.0 wt.%, with respect to the total weight of the composition.
11. Use of the at least one compound of general formula (I)



wherein

R^1 and R^2 , independently of one another, are linear or branched, substituted or unsubstituted C_1 - C_{14} alkyl;
as thickener for the at least one liquid or supercritical C_2 - C_5 hydrocarbon.

12. Use of the composition according to claim 1 for fracturing.
13. A method of fracturing a subterranean formation penetrated by a wellbore, comprising the steps of
 - (a) formulating the composition according to one or more of claims 1 to 10 with the at least one proppant to obtain a fracturing fluid, and
 - (b) pumping the fracturing fluid of step (a) down the wellbore.
14. Use of the composition according to claim 1 for enhanced oil recovery.
15. A method for enhanced oil recovery from a well bored into an oil reservoir comprising the steps of
 - (a) injecting the composition according to one or more of claims 1 to 10 into the well

- bore; and
- (b) recovering oil from the well bore.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/051550

A. CLASSIFICATION OF SUBJECT MATTER INV. C09K8/58 C09K8/64 E21B43/16 E21B43/26 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C09K E21B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SIMIC V ET AL: "Highly cooperative formation of bis-urea based supramolecular polymers", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, US, vol. 125, no. 43, 2003, pages 13148-13154, XP002388365, ISSN: 0002-7863, DOI: 10.1021/JA037589X the whole document ----- -/--	1-15
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 22 February 2019		Date of mailing of the international search report 07/03/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Nemes, Csaba A.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/051550

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FREDERIC LORTIE ET AL: "Structural and Rheological Study of a Bis-urea Based Reversible Polymer in an Apolar Solvent +", LANGMUIR, vol. 18, no. 19, 6 July 2002 (2002-07-06), pages 7218-7222, XP055371120, US ISSN: 0743-7463, DOI: 10.1021/la0255166 the whole document -----	1-15
A	WO 00/35998 A2 (UNIV YALE [US]; BECKMAN ERIC J [US]; HAMILTON ANDREW D [US]; HUANG ZHI) 22 June 2000 (2000-06-22) the whole document -----	1-15
A	US 2011/111991 A1 (SAMUEL MATHEW M [US] ET AL) 12 May 2011 (2011-05-12) the whole document -----	1-15
A	WO 2016/195713 A1 (HALLIBURTON ENERGY SERVICES INC [US]) 8 December 2016 (2016-12-08) the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/051550

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
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