A hydrate inhibitor comprising a blend of at least one of an additive (xx) and an additive (xxi) wherein additive (xx) is an ammonium salt containing at least one oxygen atom of general formula $[R_{20}NR_{21}R_{22}R_{23}]X^v$ wherein $R_{20}$ is an organic group and each of $R_{21}, R_{22}$ and $R_{23}$, which may be the same or different, represents a hydrogen atom or an organic group containing at least one oxygen atom in a hydroxyl or in an ether group, with the proviso that at least one of $R_{21}, R_{22}$ and $R_{23}$ contains at least one oxygen atom, and $X$ is an anion of valency $v$, where $v$ is an integer of 1-4 and additive (xxi) is a polyamino acid or salt thereof which has structural units derived from at least one amino acid, at least 50 % of which units have at least two carboxylic acid groups, especially polyaspartic acid.
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HYDRATE INHIBITORS

The present invention relates to hydrate inhibitors and a method for inhibiting the formation of hydrates in particular to a method for inhibiting the formation of hydrates in the petroleum and natural gas industries.

Hydrates are formed of two components, water and certain gas molecules, e.g. alkanes of 1-4 carbons, especially methane and ethane, such as those found in natural gas. These 'gas' hydrates will form under certain conditions, i.e. when the water is in the presence of the gas and when the conditions of high pressure and low temperature reach respective threshold values. The gas may be in the free state or dissolved in a liquid state, for example, as a liquid hydrocarbon.

The formation of such hydrates can cause problems in the petroleum oil and natural gas industries.

Hydrate formation in the field may cause blocked pipelines, valves and other process equipment.

The problem is particularly of concern as natural gas and gas condensate resources are discovered where operating conditions surpass these threshold values, i.e. in deep cold water and on-shore in colder climates.

Hydrates can also form in association with the underground hydrocarbon reservoir thus impeding production by blockage of reservoir pores.

The problem of hydrate formation is however commonest during gas transportation and processing, the solid hydrate precipitating from moist gas mixtures. This is particularly true with natural gas which when extracted from the well is normally saturated with water. Often in such a case, in a cold climate, hydrates will form in downstream transportation networks and this can cause large pressure drops throughout the system and reduce or stop the flow of natural gas.

Hydrate formation may also occur during natural gas cryogenic liquefaction
and separation.

A typical situation where hydrate formation can occur is in off-shore operations where produced fluids are transported in a long vertical pipeline, for example, a riser system. Such produced fluids normally include light gases known to form hydrates and water. In such a situation a temperature of 4.5°C and a pressure of 150 psi would be sufficient for hydrate formation.

Several methods are known to prevent hydrate formation and subsequent problems in pipelines, valves and other processing equipment.

Physical methods have been used, e.g. increasing gas temperature in the pipeline, drying the gas before introduction into the pipeline, or lowering the gas pressure in the system. However, these techniques are either expensive or are undesirable because of loss of efficiency and production.

Chemical procedures have also been used. Electrolytes, for example, ammonia, aqueous sodium chloride, brines and aqueous sugar solutions may be added to the system.

Alternatively, the addition of methanol or other polar organic substances, for example, ethylene glycol or other glycols may be used. Methanol injection has been widely used to inhibit hydrate formation. However, it is only effective if a sufficiently high concentration is present since at low concentrations there is the problem of facilitation of hydrate formation. Also for methanol to be used economically under cold environmental conditions there must be early separation and expulsion of free water from the well in order to minimise methanol losses in the water phase.

We have now found certain additives which may be used as effective hydrate inhibitors at low concentrations.

The present invention provides an ammonium salt [hereafter called Additive xx] containing at least one oxygen atom of general formula \([R_{20}^{+} N \ R_{21}^{\infty} R_{22}^{\infty} R_{23}^{\infty}]^{-}\)

\(X^{1/v}\) wherein \(R_{20}\) is an organic group and each of \(R_{21}, R_{22}\) and \(R_{23}\), which may be the same or different, represents a hydrogen atom or an organic group containing at least one oxygen atom in a hydroxyl or an ether group, with the proviso that at least one of \(R_{21}, R_{22}\) and \(R_{23}\) contains at least one oxygen atom, and \(X\) is an anion of valency \(v\), where \(v\) is an integer of 1-4 preferably 1 or 2.

In the Additive \((xx)\) \(R_{20}\) is an organic group e.g. of 1-24 carbon atoms especially 4-20 carbons, and in particular an organic hydrocarbyl group, such as an alkyl or alkenyl group, e.g. a linear or branched alkyl or alkenyl, such as butyl,
penty1, hexyl, 2-ethyl hexyl, decyl, dodecyl, lauryl, cetyl, palmityl, stearyl or oleyl group, or a cycloalkyl group e.g. of 5-8 carbons such as cyclohexyl, or aralkyl group e.g. of 7-20 carbons such as benzyl or aryl group e.g. aromatic hydrocarbyl such as of 6-20 carbons e.g. phenyl or tolyl. Each of R_{21}, R_{22} and R_{23} may contain a chain of carbon atoms and oxygen atom(s) of 3-10 especially 4-7 chain members. Each of R_{21}, R_{22} and R_{23} may be an aliphatic e.g. alkyl or alkenyl group, or may be a cycloaliphatic e.g. cycloalkyl group, each having at least one hydroxyl or ether substituent, or an aliphatic group having a carbon chain interrupted by at least one oxygen atom. The alkyl group with the hydroxyl or ether substituent can be of 1-24 carbons such as 1-10 especially 1-4 carbons with 1-6 e.g. 1-4 or 1-4 oxygen atoms in hydroxyl and/or ether group(s); each hydroxyl group is preferably in a primary or secondary alcohol group and especially is in a 2, 3 or 4 hydroxyl alkyl group. Examples of such hydroxyalkyl groups are 2-hydroxyethyl, 2-hydroxy-propyl or 2-hydroxy butyl. The oxygen atom of the ether substituent is preferably in the same location in the alkyl group as described for the hydroxyl group, and the ether group is preferably an alkoxy group e.g. of 1-10 carbons such as 1-6 carbons e.g. methoxy, ethoxy, propoxy, butoxy. Thus examples are methoxy- or ethoxy- or n-propoxy- ethyl or -2- or -3-propyl, or -2-, -3 or -4 butyl; preferably each of R_{21}, R_{22} and R_{23} may be an aliphatic group with a chain of 4-7 carbon and oxygen atoms. The alkyl group in the hydroxy or ether substituent can contain 1 oxygen atom preferably when each of R_{21}, R_{22}, R_{23} represents an organic group, particularly when one or two of R_{21}, R_{22} and R_{23} represents hydrogen. The alkyl group with the hydroxy or ether substituent can contain 2-6 e.g. 2 or 3 oxygen atoms, as in a polyhydroxyalkyl group such as a (trishydroxymethyl)methyl or 2,3-dihydroxy propyl group. R_{21}, R_{22} and/or R_{23} can also represent a cycloaliphatic group e.g. a cycloalkyl group with a hydroxyl or ether substituent, especially a cycloalkyl group with 5-7 ring carbon atoms e.g. cyclohexyl or cyclopentyl, and preferably a 2-hydroxy- or 2-alkoxy-1-cycloalkyl group; the ether substituent in the cycloalkyl group is usually the same as described for the ether substituent in the alkyl group. Each of R_{21}, R_{22} and R_{23} may also be an aliphatic group with at least one carbon chain interrupted by at least one oxygen atom in an ether linkage. The aliphatic group and the carbon chain may be branched (e.g. with at least one methyl or ethyl branch, especially for each oxygen atom) but preferably is linear. The aliphatic group may have a methyl group at the end of the carbon chain or a hydroxy group. The aliphatic group may be of
formula \(-(R_{24}-O)_nR_{25}\) where \(n\) is at least 1, preferably 2-25, and \(R_{24}\) is a divalent aliphatic group, e.g. of 1-10 carbons e.g. 2-4 carbons such as alkyne, e.g. methylene 1,2-ethylene, 1,2-propylene, 1,3-propylene or 1,4-butylene, and \(R_{25}\) represents hydrogen or alkyl e.g. of 1-24 or 1-10 carbons such as methyl, ethyl, propyl or butyl. Examples of the aliphatic group representing \(R_{21}\), \(R_{23}\) and/or \(R_{24}\) are 2 hydroxyethyl, 2(2-hydroxyethyl)-oxyethyl and polyethylenoxy (and the corresponding hydroxypropyl and polypropyleneoxy groups (especially with an average of 4-10 alkylene oxy units). Anion X may be monovalent e.g. a halide such as chloride or bromide, or nitrate, or divalent e.g. sulphate or carbonate or trivalent e.g. phosphate and may be inorganic or organic, e.g. a mono or divalent carboxylate e.g. from an alkan mono or di oic acid of 1-20 carbons such as acetate.

Preferred Additives xx are mono alkyl ammonium tris (hydroxyalkyl) anc. tris(polyalkylenoxy) and tris(alkoxy polyalkylenoxy) salts especially with 1-20 carbons in the monoalkyl and alklyoxy groups, 2-6 carbons in the hydroxyalkyl and each alkyleneoxy group and 1-4 alkylene oxy groups e.g. 1 or 2. Other preferred additives are monoalkyl [[tris(hydroxymethyl)]methyl] ammonium salts.

The Additives xx may be made by reaction of an amine \(R_{20}NH_2\) with a molecule containing a group capable of reacting with \(NH_2\) group to form an ammonium salt and leaving a hydroxyl or ether substituent in the salt; such reactions are known per se and described in the literature e.g. in Kirk Othmer Encyclopaedia of Chemical Technology 3rd Edition published 1982 John Wiley & Sons. Preferably the amine is reacted with an alkylene oxide to form a mono or bis (hydroxy alkyl) compound, which may be converted into an ammonium salt with an acid, or may be reacted with the alkylene oxide to form the tris (hydroxy alkyl) salt.

This reaction is described in general in said Encyclopaedia Alternatively an alkylating agent containing an \(R_{20}\) group e.g. an \(R_{20}\) halide or sulphate or sulphonate ester e.g. p-toluene sulphonate ester may be reacted with \(R_{21}R_{22}R_{23}N\) especially when \(R_{22}\) and \(R_{23}\) are hydrogen. This reaction is described in general in said Encyclopaedia.

The present invention also provided blends of Additive (xxi), and at least one of additives (i), (ii), (iii), (ix), (x), (xii), (xiii) and (xx), each as hereinafter described, especially additive (i) and/or in the substantial absence of additive (iii).

The present invention also provides blends of Additive (xx) and at least one of additives (i), (ii), (iii), (ix), (x), (xii), (xiii) and (xxi), each as hereinafter described, especially additive (i) and/or (xxi).
Additive (i) is a polymer of (a) an ethylenically unsaturated N-heterocyclic carbonyl compound, with 6-8 ring atoms in the heterocyclic ring and optionally (b) a different ethylenically unsaturated N-heterocyclic carbonyl compound with 5-7 ring atoms in the heteroring, the numbers of heteroring atoms in (a) and (b) differing by at least one. Additive (ii) is a corrosion inhibitor and Additive (iii) is a salt which is of formula \([R^1(R^2)X^1R^3]^+Y^-\)/\(\nu\), wherein each of \(R^1\), \(R^2\) and \(R^3\) is bonded directly to \(X^1\), each of \(R^1\) and \(R^2\), which may be the same or different is an alkyl group of at least 4 carbons, \(X^1\) is S, NR\(^4\) or PR\(^4\), wherein each of \(R^3\) and \(R^4\) which may be the same or different represents hydrogen or an organic group, with the proviso that at least one of \(R^3\) and \(R^4\) is an organic group of at least 4 carbons, especially at least 5 carbons, and \(Y\) is an anion of valency \(\nu\), wherein \(\nu\) is an integer of 1-4 e.g. 1 or 2.

The present invention also provides a method of inhibiting or retarding hydrate formation and/or growth, which method comprises adding Additive (xx) or a blend of the invention in amount effective to inhibit or retard hydrate formation or growth to a medium susceptible to hydrate formation.

The Additive (i) is a Polymer of (a) and optionally (b), each being ethylenically unsaturated N-heterocyclic carbonyl compounds. The weight proportions of structural units from (a) to (b) may be 100:0 or 100-40:0-60, such as 100-60:0-40 or preferably 100-85:0-15, preferred proportions are 100:0, 50:50 and 75:25. The Polymer has a hydrocarbon chain with pendant N-heterocyclic carbonyl groups, with the bonding to the chain preferably via the heteroring -N- atom.

The Polymer may be made by polymerisation of (a) or simple copolymerisation of (a) and (b) or may be a graft copolymer, e.g. from grafting (b) onto homopolymeric (a). Each N-heterocyclic carbonyl compound may contain 1 or more than 1 e.g. 2 or 3 heterocyclic rings, but each case it contains at least 1 ring containing the specified number of ring atoms. That N heterocyclic ring may contain 1-3 ring N atoms but especially 1 ring N atom and 0-2 other ring hetero atoms e.g. 0 or S, but especially no extra ring hetero atom. The ring or rings may be saturated or ethylenically unsaturated. The carbonyl group may be in any position in the N heteroring, but is especially alpha to the N hetero atom, so the N-heterocyclic rings are preferably derived from lactams, such as those derived from butyric, pentenoic, pentanoic or hexanoic acid lactams (or 2-pyrolidone, 2-pyridone, 2-piperidone or omega caprolactam). The polymer may have structural
units from N-vinyl omega caprolactam (and be a homopolymer) or may also have structural units from N-vinyl pyrrolidone.

The polymer preferably consists essentially of structural units derived from (a) e.g. homopoly caprolactam or consists essentially of structural units from (a) and only ethylenically unsaturated N-heterocyclic compounds especially (b); structural units from polar ethylenically unsaturated non cyclic compounds (especially from esters of an alcohol containing more than 1 polar group and an unsaturated acid) and/or ethylenically unsaturated carbocyclic carbonyl compounds are preferably substantially absent.

Preferably the Polymer is water soluble or water dispersible, e.g. to an extent of at least 0.01% by weight in water such as at least 0.05% but especially at least 0.5%, such as up to 10% by weight. Its molecular weight is usually 5,000 to 1,000,000 e.g. 10,000 to 1,000,000 such as 1,000 to 50,000 or 50,000-500,000 and preferably has a K value of 10-150 especially 15-50, wherein the K value is obtained from the relative viscosity in aqueous solution via the FIKENTSCHER'S Formula, from which the average molecular weight is calculated as described in USP2,811,499.

The polymers may be as described in WO 94/12761, the disclosure of which is herein incorporated by reference.

The blend of the invention can comprise at least one of Additive (ii) which is a Corrosion Inhibitor and (iii) the salt of formula I. The blends may comprise both (ii) and (iii), or may comprise (ii) in the substantial absence of (ii), or (iii) in the absence of more than 2% of (ii) (based on the combined weight of Additives (i) and (iii), preferably in the substantial absence of (ii).

The Additive (ii) is a corrosion inhibitor eg. for steel and usually one suitable for use in anaerobic environments. It may be a film former, capable of being deposited as a film on a metal eg. a steel surface such as a pipeline wall. It preferably has surfactant activity and especially surface wetting activity.

It is especially a nitrogenous compound with 1 or 2 nitrogen atoms. The corrosion inhibitor may be a primary, secondary or tertiary amine, or a quaternary ammonium salt, usually in all cases with at least one hydrophobic group, usually a benzene ring or a long chain alkyl group eg. of 8-24 carbons. It may be a quaternary ammonium salt, a long chain aliphatic hydrocarbyl N-heterocyclic compound or a long chain amine. The quaternary salt may be an (optionally alkyl substituted) benzyl trialkyl ammonium halide, in particular when at least 1 and
especially 1 or 2 alkyl groups is of 1-20, in particular 8-20 carbons such as cetyl and the other alkyl groups are of 1-6 carbons such as methyl or ethyl; examples are benzyl alklyldimethyl ammonium chloride and Benzalkonium chlorides e.g. mixtures of benzyl alklyldimethyl ammonium chlorides wherein each alkyl has 8-20 carbons especially 8-18 or 12-18 carbons.

Other quaternary ammonium salts may be of formula [R⁵R⁶NR⁷R⁸]⁺Z⁻₁/ₚ, wherein Z is an anion e.g. a halide or sulphate and w is an integer of 1-4 e.g. 1 or 2, R⁵ is an alkyl or alkenyl group of at least 8 carbons, R⁶ is an alkyl or alkenyl group, each of at least 2 carbons or a N- heterocyclic group, and R⁷ and R⁸, which may be the same or different represents an alkyl group, with the proviso that at least one of R⁶ - R⁸ has less than 4 carbon atoms. R⁵ may be of 8-24 carbons, such as 10-18 carbons, especially, dodecyl, lauryl, cetyl, palmityl, stearyl or oleyl, while R⁶ may be selected from the same groups as R⁵, or may be ethyl, propyl, isopropyl, butyl or hexyl. R⁷ and R⁸ may be selected from the same groups as R⁶ but preferably represent methyl groups. Examples of these quaternary salts are cetyl trimethyl ammonium, dodecyl trimethylammonium and lauryl trimethylammonium halides, e.g. chlorides or bromides.

Other quaternary salt corrosion inhibitors are of formula [R⁹NR¹⁰R¹¹]⁺Z⁻₁/ₚ where Z is a anion as defined above and w is an integer of 1-4 e.g. 1 or 2, R⁹N or R⁹NR¹⁰ forms a quaternizable N heterocyclic ring, and R¹¹ represents an alkyl or alkenyl group each of at least 8 carbons e.g. as described for R⁵. The R⁹N group may be N- heterocyclic group with 1 or 2 ring N atoms, especially with 1 or 2 heterocyclic rings, e.g. of 5 or particularly 6 ring atoms, examples of the rings are saturated ones e.g. piperidine. The group R⁹NR¹⁰ may also be such an N heterocyclic group but with the R⁹ and R¹⁰ groups combined with the N atom to which they are bonded to form an unsaturated ring or fused N bridged ring system such as a pyridine ring. R¹⁰ if present may otherwise be an alkyl or alkenyl group e.g. as described for R⁸. Examples of these quaternaries are cetyl pyridinium halides, such as the chloride.

The corrosion inhibitor may also be a long chain aliphatic hydrocarbyl N-heterocyclic compound, which is not quaternised. The aliphatic hydrocarbyl group in the heterocyclic compound usually has 8-24 carbons in the hydrocarbyl group, preferably a linear saturated or mono or diethylenically unsaturated hydrocarbyl group; cetyl-, stearyl and especially oleyl- groups are preferred. The N- heterocyclic compound usually has 1-3 ring N atoms, especially 1 or 2 which
usually has 5-7 ring atoms in each of 1 or 2 rings; imidazole and imidazoline rings are preferred. The heterocyclic compound may have the aliphatic hydrocarbaryl group on an N or preferably C atom in the ring; the ring may also have an aminoalkyl (e.g. 2-amino ethyl) or hydroxyalkyl (e.g. 2-hydroxyethyl) substituent, especially on an N atom. N-2-aminoethyl-2-oleyl-imidazoline is preferred. The long chain amine usually contains 8-24 carbons and preferably is an aliphatic primary amine, which is especially saturated or mono ethylenically unsaturated; an example is dodecylamine. Mixtures of any of the above corrosion inhibitors with each other may be used, eg a quaternary ammonium salt and a long chain aliphatic hydrocarbaryl-N-heterocyclic compound (where each is preferably as described above), or mixtures with a tertiary aliphatic amine.

If desired the corrosion inhibitor eg. a long chain amine may also compr se a phosphate ester salt, especially one with surface wetting activity. Such phosphate esters are anionic surfactants, which are salts of alkali metals eg. sodium or a quaternary ammonium eg. tetra methyl ammonium or tetrabutyl ammonium salts of acid phosphate esters, eg. with 1 or 2 organic groups and 2 or 1 hydrogen atoms; examples of the organic groups are alkyl or alkenyl groups as described for R⁵ above. Examples of such phosphate ester salts are mono and dioctyl acid phosphate salts and mixtures thereof. A preferred blend comprises a long chain alkylamine and a phosphate ester salt eg. as sold as NAL 1272 by Nalco. Other corrosion inhibitors include blends of a phosphate ester salt and an inorganic salt, usually with water and a glycol ether e.g. butyl diglycol ether such as is sold by BP Chemicals under the Trade Mark C795.

Additive (iii) is a salt of formula I, [R¹R²X¹R³]⁺Y⁻1/v, in which each of R¹ and R² is an alkyl group of at least 4 carbons, which may be a linear alkyl or branched alkyl group, eg. a secondary or tertiary alkyl group or especially an isoalkyl group. Each of R¹ and R² may be an alkyl group of 4-24 carbons, preferably 4-10 and especially 4-6 carbons, such as n-butyl, isobutyl, secbutyl, tertiary butyl, n-pentyl, sec pentyl, isopentyl or tertiary pentyl group, or hexyl group. R³ and R⁴ (if present as is preferred) are each hydrogen or an organic group eg. of 1-24 carbons such as an alkyl or alkenyl group each preferably of 8-20 carbons, eg. as is described for R⁵ above; however at least one or R³ and R⁴ contains at least 4 carbons eg. at least 5 carbons, especially in a group with a linear chain containing such numbers of carbon atoms. R³ may preferably be an alkyl group of 10-16 carbons, especially a mixture of 2 or more such alkyl groups. R⁴
may be hydrogen but is preferably alkyl of 1-10 carbons, eg. methyl or ethyl but especially of 4-6 carbon atoms, such as is described for \( R^1 \) or \( R^2 \). \( Y \) is an anion e.g. selected from those described or \( X \) and \( Z \) above. Preferred salts are tetra n-butyl, tetra n-pentyl, tetra-iso-pentyl ammonium (and phosphonium) halides eg. chlorides or especially bromides, and \( C_{10-16} \) alkyl tri n-butyl ammonium (and phosphonium) halides, especially chlorides or bromides. Tri n-butyl, n-pentyl or isopentyl sulphonium halides eg. chlorides or bromides may be used.

Additive xx and (i) may be present in the blends of the invention in weight ratios of 10-90:90-10 preferably 40-70:60-30, especially with at least an equal weight of \( \text{xx} \) to (i). Additive xx and (ii) may be present in the blends in weight ratios of 10-90:90-10 preferably 30-70:70-30.

The Additives (i) and (ii) may be used in weight ratios of 25:0.5-20 e.g. 25:0.75-15 especially 25:1.5-15 or 25:3-12 or 25:3-7, while the weight ratio of Additives (i) and (iii) may be 25:3-50 e.g. 25:15-40. When Additives (i), (ii) and (iii) are present, the relative weight ratios may be 25:0.5-20 : 3-50, such as 25:1.5-15 : 15-40. The Additives may be used in amounts to provide 500-4000ppm Additive xx, 0 or 500-4000ppm, e.g. 1000-4000ppm Additive (i), 0 or 50-2000 e.g. 150-2000ppm especially 300-700ppm Additive (ii) and 0 or 400-4000ppm Additive (iii) (based on the total weight of water present in the medium), preferably with total amounts of Additives (xx and (i)/(ii)/(iii) as present) of 1500-8000 e.g. 4000-7000ppm (on the same basis).

The Additives (ii) and (iii) may themselves be present in weight ratios of 1-99:99:1 such as 10-90:90:10, but especially with a weight excess of Additive (iii) such as with a ratio of (ii) to (iii) of 10-45:90-55.

The Additives (ii) and (iii) for use as hydrate inhibitors are preferably water soluble, e.g. to at least 10 g/l in water at 20°C. They may be used undiluted, but preferably are in solution such as aqueous solution, for example, as a solution in brine, or preferably an alcohol, for example, a water miscible one such as methanol or ethanol. Preferably are used Additives (ii) and (iii), an aqueous solution of which has a pH 1.5-12, e.g. 4-9, either naturally or after adjustment of the pH. Additives (ii) and/or (iii) may be used in alcoholic solution. Each Additive is suitably injected at concentrations in the range 10 to 20,000 ppm, e.g. 30 to 10,000 ppm, especially 50-1200 ppm based on the total water volume in the medium, in which hydrate formation is to be inhibited, in particular at concentrations in the range 200-1500 ppm for Additive (ii) and 500-5000 ppm for Additive (iii).
amount of methanol, ethanol, or mono, di or tri ethylene glycol added that may be added (but is preferably absent) relative to the total water volume in the medium is usually less than 10%, e.g. less than 5% or 2%, but especially less than 10,000 ppm, eg 1000 - 8000 ppm.

The inhibitors may be injected at normal ambient conditions of temperature and pressure.

There may also be present with the Additive (xx) and/or (xxi) at least one Additive (ix) which is at least one water soluble polymer of a polar ethylenically unsaturated compound and/or at least one Additive (x) which is a hydrophilic colloid, Additive (ix) being different from Additive (i). The Additive (ix) is usually water soluble to at least 10 g/l at 20°C and advantageously has a molecular weight of 1000-1500,000, e.g. 5000-1,000,000, preferably 200,000-1,000,000 and especially 400,000-900,000. The ethylenically unsaturated compound is preferably a vinyl or methyl vinyl group, and the polar group may be an alcohol, carboxylic acid, sulphonic acid or N-heterocyclic group, especially pyrrolidone. Preferred polar compounds are thus vinyl sulphonic acid, acrylic and methacrylic acids and N-vinyl pyrrolidone and "vinyl alcohol". The polymers may be copolymers, but are preferably homopolymers of these polar compounds, especially polyvinyl alcohol (e.g. hydrolysed polyvinyl acetate), polyacrylates and polyvinyl pyrrolidone (PVP).

The amount of said polymer Additive (ix) is usually 10-1000%, such as 50-300% or 90-250% based on the weight of the total of Additive(s) xx, (xxi), (i), (ii) and (iii) as present.

The hydrophilic colloid (x) is an organic solid which is soluble in boiling water, e.g. to at least 10 g/l or dispersible in boiling water and may be soluble (at least 10 g/l) or dispersible in water at 20°C. It usually absorbs water strongly, e.g. to at least three times such as 3-15 times its weight of water at 20°C, and swells in water. It can form a colloidal solution or dispersion in water and may have an average molecular weight of at least 10,000, e.g. 100,000-10,000,000. It may be a polysaccharide, e.g. with at least 4 carbohydrate units, especially one with at least some galactose units, e.g. 20-60% of such units, and may contain carboxylic acid residues, so that an aqueous solution or dispersion thereof can have an acidic reaction. The polysaccharide may be a natural gum, e.g. guar, agar, arabic, locust bean, karaya, carob or tragacanth gum, or a cellulosic material, such as starch, which may be unmodified or modified as an alkyl ether, e.g. methyl or ethyl cellulose or hydroxyalkyl ether, e.g. hydroxyethyl cellulose or carboxy alkylated
starch, e.g. carboxy methyl cellulose (CMC). The polysaccharide may also be a synthetic, e.g. biosynthetic gum, the result of a microbiological process, e.g. fermentation; xanthan gum, which can be made by fermentation of dextrose with Xanthomonas campestris cultures, which is preferred, especially water soluble versions of xanthan gum. The colloid may also be proteinaceous, in particular gelatin or carrageenan (a seaweed extract), e.g. x-carrageenan. The colloid may also be a polyuronic acid or salt thereof, e.g. sodium or ammonium salt or ester thereof, such as a hydroxy alkyl ester (e.g. of propylene glycol), especially with beta-D-mannuronic acid residues; alginic acid and especially sodium alginate is preferred. The amount of Additive (x) may be 10 - 1000%, eg 50 - 300% or 90 - 250% by weight based on the total weight of Additives (xx), (xxi), (ii), (iii) as present.

There may be present the Polymer as Additive (xii) with an aliphatic (N-heterocyclic carbonyl) polymer with a hydrocarbon backbone. It is water soluble or water dispersible, eg to an extent of at least 0.01% by weight in water such as at least 0.05% but especially at least 0.5%, such as up to 10% by weight. Its molecular weight is usually 5000 to 1000000 eg 10000 to 1000000 such as 1000 to 50000 and preferably has a K value of 10 - 150 especially 15 - 50, wherein the K value is obtained from the relative viscosity in aqueous solution via the FIKENTSCHER'S Formula, from which the average molecular weight is calculated as described in USP 2,811,499. The Polymer has a hydrocarbon chain with pendant N-heterocyclic carbonyl groups, with the bonding to the chain via the heteroring -N- atom and the N-heterocyclic carbonyl groups as described further above. The aliphatic group or groups in the polymer may be part of the hydrocarbon chain, or bonded to it or to the N-heterocyclic carbonyl ring; the aliphatic group may be linear or branched and maybe alkyl eg of 1 - 40 eg 2 - 25 carbons or alkenyl eg of 2 - 20 carbons, especially methyl, ethyl, butyl or octyl, tetradecyl, hexadecyl, octadecyl, eicosyl, tricosyl or ethylene, butylene or octylene. The molar ratio of aliphatic group to heterocyclic carbonyl group in the Polymer is usually 1:99 to 20:80 eg 5 : 15 : 95-85.

The Polymer may be a copolymer having repeat units derived from at least one monomer which is an optionally alkyl substituted vinyl N-heterocyclic carbonyl compound) and at least one monomer which is an olefin, this copolymer may be simple copolymer formed by copolymerization of the monomers or a graft copolymer formed by grafting the olefin onto a polymer of the N-heterocyclic
monomer. The Polymer may also be an alkylated derivative of a polymer of an
optionally alkyl substituted (vinyl N-heterocyclic compound) especially a
homopolymer of such a compound.

The optionally alkyl substituted vinyl N-heterocyclic carbonyl compound
may be of general formula:

\[ R^{12} R^{13} C = CR^{14} R^{15} \]

wherein each of \( R^{13}, R^{14} \), and \( R^{15} \), which may be the same or different, represents
a hydrogen atom or an alkyl group eg of 1 - 20 carbons, such as methyl, ethyl,
butyl, hexyl, decyl or hexadecyl, and \( R^{12} \) represents an N-heterocyclic carbonyl
group with the free valency on the N atom; preferably the N heterocyclic carbonyl
group is as described above. The N-heterocyclic ring may contain 1-3 ring N
atoms but especially 1 ring N atom and 0 - 2 other ring hetero atoms eg 0 or 5, but
especially no ring hetero atom; the ring may contain in total 1 or 2 rings, which
may be saturated or ethylenically unsaturated such as a pyrrolidine, piperidine,
quinoline or pyridine ring. Preferably \( R^{13}, R^{14} \) and \( R^{15} \) are hydrogen and \( R^{12} \)
represents an N-(pyrrolidone), N-(2 pyrid-2-one) or N-(piperid-2-one) group.

The olefin is usually of 2 - 32 eg 4 - 18 carbon atoms and is generally a
hydrocarbon. It is preferably an alkene, especially a linear alkene and has in
particular a terminal olefin group. It is preferably a vinyl olefin eg of formula CH\(_2\
= CH - R^{16} \), where \( R^{16} \) is hydrogen or alkyl of 1 - 40 carbons, such as methyl,
ethyl, propyl, butyl, hexyl or decyl, tetra decyl, octadecyl or octacosyl (so the
olefin is tricosene). The olefin is preferably butylene octene-1 or dodecene-1, hexa
decene-1, octadecene-1, eicosene-1 or tricosene-1.

The Polymer may be made by free radical copolymerizing the N-
heterocyclic carbonyl compound eg N-vinyl pyrrolidone with the olefin eg butylene
in solution in the presence of a peroxide catalyst. The Polymer may also be made
by free radical grafting of the olefin onto a polymer of the N-heterocyclic carbonyl
compound eg poly vinyl pyrrolidone (PVP) with K value as described above. The
copolymerizations may incorporate structural units from the olefin into the
hydrocarbon polymer chain and/or insert such units into the N-heterocyclic rings.

The Polymer may also be made by direct alkylation of the polymer of the
N-heterocyclic carbonyl compound eg PVP with an alkylating agent eg an alkyl
halide such as butyl bromide or octyl bromide, optionally in the presence of a base,
such as triethyl amine.

Finally the Polymer may be a homo or copolymer of an alkyl substituted N-
(alkenyl) heterocyclic compound in which the alkyl substituent may be in the N-heteroring and/or present in the alkenyl side chain; the alkyl substituent may be as is preferred for the aliphatic group on the Polymer described above. The Polymer may have structural units from an N-vinyl-alkyl ring substituted heterocyclic carbonyl compound, such as N-vinyl-3-methyl pyrrolid-2-one and/or from an N-butenyl-heterocycle carbonyl compound, such as N-butenyl-pyrrolid-2-one. Such Polymers may be made by polymerization in solution in the presence of a free radical catalyst, in an analogous way to polyvinyl pyrrolidone.

Thus the preferred Polymers are aliphatic (N-heterocyclic carbonyl) polymers with units derived from N-vinyl pyrrolid-2-one and butylene (sold as Antaron P 904), octylene, dodecylene, hexadecylene (sold as Antaron V216), eicosylene and tricosylene; the Antaron products are sold by International Speciality Products of Wayne, N.J., USA. Polymer xii may be as described in WO 93/25798 the disclosure of which is herein incorporated by reference.

The Polymer may also be as Additive (xiii) a copolymer of (a) at least 1 ethylenically unsaturated N- heterocyclic ring compounds especially with at least one of (b) a different ethylenically unsaturated N-heterocyclic ring compound, (c) an ethylenically unsaturated carbocyclic carbonyl compound, and (d) a polar ethylenically unsaturated compound, different from said N-heterocyclic compounds, said copolymer being different from Additive (i). Polymer Additive xiii preferably consists essentially of structural units derived from at least 2 of said (a)-(d) compounds, in particular (a), (b) and (d). Polymers (xiii) from heteroring ring compounds with different size rings e.g. with differences of 1-3 in the numbers of ring atoms are preferred, especially ones with 5 and 7 membered heterorings.

Examples of the ethylenically unsaturated N-heterocyclic ring compounds are ones described above in relation to Polymers (i), (xx) especially N-vinyl-pyrrolidone and N-vinyl omega caprolactam. The carbocyclic compound may be one with 4-8 e.g. 6 or 7 ring atoms with the carbonyl group in the ring preferably adjacent to a carbon atom carrying the ethylenically unsaturated group which is preferably an alkenyl group of 2-6 carbon atoms especially with a terminal \( \text{CH}_2=\text{CH}- \) group. The carbocyclic compounds are cyclic ketones with an unsaturated side chain. Examples of the carbocyclic compound are 2-vinyl- cyclohexanone and 2-vinyl-cycloheptanone. The polar ethylenically unsaturated compound may be an ester of an alcohol containing more than 1 polar group and an unsaturated acid. The alcohol usually contains a hydroxyl group and at least one other hydroxyl group or
aminogroup, which may be a primary secondary or especially tertiary amino group in particular in a non cyclic arrangement; thus the alcohol may be a diol or an amino alcohol, especially an aliphatic one, such as a dialkylaminoalkanol, with 1-4 carbons in each alkyl and 2-4 carbons in the alkanol. 2-Dimethylamino ethanol is preferred. The unsaturated acid is usually an aliphatic alkenoic acid with 3-10 carbons such as acrylic or methacrylic or crotonic acid. This unsaturated ester is especially a (meth) acrylate ester of a dialkylamino alkanol in particular dimethylaminoethyl acrylate or methacrylate. Polymer Additive xiii may be as described in WO94/12761, the disclosure of which is herein incorporated by reference.

The Polymer (xiii) may contain structural units in molar % derived from 10-90% of the N-heterocyclic compound. 10-90% of the carbocyclic compound and 10-90% of the polar ethylenically unsaturated compound. A preferred compound is a copolymer of N-vinyl pyrrolidone, N-vinyl-omega caprolactam and dimethylamino ethyl methacrylate, such as is sold as Antaron VC713 by International Speciality Products of Wayne, NJ.

The amount of said Polymer (xiii) is usually 10-1000% such as 50-300%, 90-250% or 20-50% based on the weight of the total of Additives (xx), (xxi), (i), (ii), (iii) as present. Mixtures of the aliphatic (N-heterocyclic carbonyl) polymer (xii) and the copolymer (xiii) may be used especially in weight ratios of 10-90:90-10 in particular a majority of (xiii) eg. in weight ratio of (xii) to (xiii) of 10-40:90-60.

 Preferably at least one and preferably all of Additives ix, xii and xiii are substantially absent from the blends and methods of the invention. as such blends are then of reduced toxicity. Additive (x) may also be absent.

The Additive (xxi) is a polyamino acid or salt thereof which has structural units derived from at least one amino acid, e.g. amino acids, at least 50% of which have at least two carboxylic acid groups e.g. 2-4 such as 2-3 groups. Preferably at least 90% of the amino acid units have at least 2 carboxylic groups and especially substantially all of them. The other amino acid structural units, if any, may be neutral or basic amino acids e.g. glycine or any amino acid as described as Additive (i) in WO94/24413, the disclosure of which is herein incorporated by reference; preferably the other amino acid(s) is basic, with linear or cyclic basic side chains and may be histidine, proline or ornithine, or less preferred lysine or arginine. The amino acids may be alpha or beta amino acids and may be optically active in D or L.
form or racemic. Each amino acid with at least 2 carboxylic groups may have a carboxyalkylene side chain e.g. of formula HOOC(CH$_2$)$_d$- where d is 1-3, especially 1 such as aspartic or 2 such as glutamic acid. The polyamino acid may have structural units derived substantially from aspartic acid or glutamic acid or both.

The polyamino acid may have a backbone with alpha carboxy amide group (i.e. via the amino and alpha carboxyl group) and/or beta carboxy amide or gamma carboxyamide groups (i.e. via the amino and a beta or gamma carboxylic acid group), preferably with a backbone at least some of which is in a beta carboxyamide form. The polyamino acid preferably has a backbone comprising aspartic acid structural units, bonded via a mixture of alpha and betacarboxyamide groups e.g. in molar ratio of 10-90:90-10 especially 10-50:90-50. Such a polyamino acid with mixed backbone bonding may be made by ring opening of poly (succinimide) e.g. by hydrolysis in the presence of a catalyst such as a base e.g. at 50-100°C. The poly succinimide may be made by heating aspartic acid or amino succinic acid (or succinimide, itself from ammonia and maleic anhydride. Further details of these reactions are given in EP 578448, US 5219952 and 5116513, and Macromolecules (1994), 27(26) pp 7613-20, the disclosure of which is incorporated herein by reference. The polyamino acids with some non acidic side chains may be made by reaction of the non acidic amino acid (as an ester) with a polyamino acid with only carboxyl side chain, or with a precursor therefor e.g. polyalpha amino succinimide, block copolymers may thus be formed. Random copolymers may be formed from a mixture of the esters of the various amino acids. The polyamino acid salts may be alkali or alkali earth metal salts, especially water soluble ones, such as sodium potassium, magnesium or calcium salts.

The polyamino acid may also contain a small amount e.g. up to 10% molar of structural units with side chains containing a carboxyamide group e.g. as in aspartic amide or glutamidc and/or a small amount e.g. with up to 10% molar of the structural units containing a cyclic imide e.g. with the carbonyl group condensed with a backbone amide nitrogen atom, as in incompletely ring opened polyamino succinimide. The polyamino acid usually consists substantially of structural units derived from amino acids. Preferably the polyamino acid has a weight average molecular weight of 1000 - 100,000 such as 1000-50,000 e.g. 1000 - 6000 or 10,000 - 30,000 and Molecular Weight Distribution i.e. Mw/Mn of 1-10 e.g. 1.5-3. Advantageously the polyamino acid is polyaspartic acid (as such or in an alkali metal e.g. sodium salt form) or its precursor (with a small percentage of aspartic
units in imide form).

The weight ratio of Additive xx to xxi may be 10:90 to 99:1 e.g. 40:60 to 95:5 such as 70:30 to 95:5 or 75-90:25-10 or 40:60 to 60:40. The weight ratio of each of Additives (i), (ii), (iii), (ix), (x), (xii) and (xiii), if present, especially (i), to Additive xxi may be 10:90 to 99:1 e.g. 50:50 such as 70:30 to 95:5 such as 75-90:25-10 or 90:10 to 99:1. Preferred blends of Additive (xxi) are (a) with Additive (xx), alone or with Additive (i), or (b) with Additive (i), or (c) with additives (iii), (xii), (xiii). Such blends (a) and (b) may contain 300-3000 parts Additive (xxi) 0 or 1000-3000 parts Additive (xx), and 0 or 1500-6000 parts Additive (i), while blend (b) may contain 10-600 e.g. 20-500 or 70-400 or especially 90-350 or 150-300 parts Additive (xxi) and 1500-6000 parts Additive (i). Blends (c) may contain 7)-300 parts Additive (xxi), 400-3500 parts of either or each of additives (iii) and (xiii) (and especially 2000-4000 parts in total of (iii) and (xiii as present) and 200-1000 parts of additive (xii). Total amounts of Additives (xxi) and (i)//ii/xii/xiii and xx as present are 2500-8000ppm, e.g. 3000-4500 or 4500-6500ppm (based on the total weight of water present in the medium). The amount of Additive xxi may be 50-5000 e.g. 50-600 (such as 80-400 preferably 120-350) or 1000-3000ppm (relative to the total weight of water in the medium). Additive xxi may be used in the presence or absence of Additive (i) or (ii).

The Formulations and blends preferably contain at least one anti-foaming agent (xiv) especially when the Additive (xx), (ii) or (iii) has foaming activity, e.g. when either contains at least one alkyl group of at least 8 carbon atoms. Examples of suitable anti-foaming agents are silicon containing compounds especially organosilicon oxygen or nitrogen compounds, such as polysiloxanes, including cyclic polysiloxanes, silicon polyethers, polysilazanes and fluorosiloxanes. Alkylpolysiloxanes are preferred especially dimethyl polysiloxanes such as 3556 from Th. Goldschmidt KG and AF 1520 from Dow Corning. The silicon anti-foaming agents are usually used as water dispersible emulsions. Silicon free anti-foaming agents, such as suds depressants used in detergents, may also be used. The amount of the anti-foaming agent is usually 10-70ppm e.g. about 40ppm (based on the total water present), or 0.1-5% e.g. 0.5-3% (based on the total weight of Additives (xx), (xii), (i), (ii) and (iii) as present).

Formulations comprising Additive (xx), (xii), (i), (ii) and/or (iii) and optionally at least one of Additive (ix), (x), (xii), (xiii) and (xxi) may be used in total amount of 50-10,000 ppm, especially 150-2000 ppm, or 2000-8000 such as
4000-6000 ppm relative to the total water in the medium in which hydrates may form (including any water added in the formulation).

The Formulation may also contain another hydrate inhibitor and/or a water dispersant or surfactant, in particular an anionic one such as sodium dodecyl sulphonate or stearic acid and in amount of 1-10% of the Formulation weight and/or a biocide, e.g. formaldehyde, e.g. in amount of 10-10,000 ppm and/or a metal complexant such as citric acid (e.g. in amount of 10-10,000 ppm) all amounts being in relation to the total weight of the Formulation.

The Formulations may be used to retard or inhibit hydrate formation and may also reduce the rate of crystal growth of gas hydrates.

The inhibitor Formulations of the present invention are suitable for use in media containing water and gas, in particular in the petroleum, natural gas and gas industries. The gas may be a hydrocarbon normally gaseous at 25°C and 100 KPa pressure, such as an alkane of 1-4 carbon atoms eg methane, ethane, propane n or isobutane, or an alkane of 2-4 carbon atoms eg ethylene, propylene, n- or isobutene; the gas preferably comprises by weight (or especially by moles) at least 80% and especially at least 90% of methane with 0.1 - 10% eg 1-5% C2 hydrocarbon and/or 0.01 - 10% eg 0.05 - 5% C3 hydrocarbon. A natural gas, which may or may not have been purified or processed is preferred. The gas may also contain nitrogen eg in amount of 0.01-3% by weight and/or carbon dioxide eg in amount of 0.1 - 5% such as 0.5 - 2% or 1-5% by weight. The formulations of the invention are particularly suitable for treating wet gases, whose composition (on a dry basis) comprises (by moles) 80-90% methane, 3-8% ethane, 1-5% propane and 0.5-3% C4 and C5 hydrocarbons, as well as 1-5% carbon dioxide and 0.1-1.5% nitrogen, these gases being particularly prone to producing gas hydrates. The Additive (xx) alone or especially with (i), (ii) and/or (iii) or additive xxi with xx/(i)/(ii)/xiii/xiii (as present) can be more effective than poly vinyl pyrrolidone in the inhibition of gas hydrate formation, especially when the gas comprises carbon dioxide.

In particular, they may be suitable for use during the transportation of fluids comprising gas and water eg from oil or gas wells. They may also be suitable for use in oil based drilling muds to inhibit hydrate formation during drilling operations.

In another aspect therefore the invention provides an oil based drilling mud, which comprises as hydrate inhibitor at least one Additive (xx), as such or in a
Formulation.

When used during the transportation of fluids, e.g. gases with water and optionally oil, e.g. condensate in conduits such as pipelines the inhibitors may be injected continuously or batchwise into the conduit upstream of conditions wherein hydrate formation may occur. Conditions under which gas hydrates may form are usually at greater than -5°C eg greater than 0°C such as 0 to 15°C eg 1 - 10°C and pressures eg of 0.1 - 30 MPa eg 1 - 15 MPa the temperature of onset of gas hydrate formation depending on the pressure, and the presence of, and concentration of, salt in the water. As the temperature decreases and the pressure increases and the concentration of salt decreases the greater is the likelihood for hydrate formation to happen in the absence of the Additives and Formulations of the invention. Thus the conditions of use of the Formulations are ones such that in their absence a gas hydrate may form, or crystals of gas hydrate may grow. In the absence of the Formulations ice may also form in addition to the gas hydrate especially at temperatures of -5°C to 5°C. The pH of the water eg in the pipeline after addition of the Formulation is usually 3-9, especially 3.3-5 or 5-7.5.

In drilling operations the inhibitors may be added to the drilling muds in the mud tank at the wellhead.

The invention is illustrated in the following Examples.

Examples

To assess the efficiency of hydrate inhibitors suitable for use in the method of the present invention, tests were carried out using the following procedure:

The hydrate inhibitor test apparatus consisted of a simple 316 stainless steel pressure cell, with a usable internal volume of 1000 cm$^3$ with a thermostated cooling jacket, a sapphire window, an inlet and outlet and a platinum resistance thermometer. The cell contained water which was stirred by a magnetic pellet. Temperature and pressure were monitored and the results provided on a computer data logger; gas hydrates were also detected visibly using a time lapse video recording system. Before each test the cell was cleaned thoroughly by soaking successively in 10% aqueous hydrochloric acid for 1 hour, 10% aqueous sodium hydroxide solution for 1 hour and then double distilled water.

Into the cell was placed 200 cm$^3$ of pre-chilled double distilled water with or without the chemical to be tested. A PTFE stirrer pellet was then placed in the cell and the pH of the solution measured with subsequent adjustment if desired by
the addition of small but concentrated amounts of hydrochloric acid or sodium hydroxide. After sealing the cell the water was then stirred at 500 rpm and allowed to cool to the operational temperature of 4°C. When this temperature was reached the stirrer was stopped and the video recorder started. A gas mixture of 2% propane and 98% methane (by moles) was then admitted to the cell until the pressure reached 70 bar (7 MPa) and the temperature, pressure and time were noted. The stirrer was restarted to run at 500 rpm and the time noted. Hydrates were observed to form in the vessel when the solution in the vessel turned opaque, coincident with which was a sharp temperature increase of about 0.2°C and a gradual pressure reduction. The time from first contact of water and gas to formation of hydrate was read from the logger.

The experimental conditions are very severe and accelerated test of gas hydrate formation and inhibition. The amounts of the Additive are expressed in ppm based on the volume of water. The inhibition time results given are an average of several results.

In the Examples, the following Additives were used:

Additive (i) was homopolymeric N-vinylomega caprolactam, which was a water soluble polymer obtained as about 52% solutions in methanol from International Speciality Products of Wayne NJ, USA under the Trade Mark ACP 1177, and with weight average molecular weights of about 75,000.

Additive (xiv) was an anti-foaming agent, which was a polydimethylsiloxane sold by Dow Corning under the Trade Mark AF1520.

Additives xx(a) and (b) were as made in Examples 1 and 2 respectively.

Additive (xxi) was a poly-DL-aspartic acid sold by Rohm and Haas, USA, which is a polyamino acid consisting essentially of DL aspartic acid structural units, which are bonded together via the amino group and the beta and alpha carboxyl groups in about a 75:25 weight ratio. The Weight Average Molec. Wt. of Additive (xxi) was 22,200 and its Mw/Mn was 1.95.

Additive (iii)a was tetra-n-butylammonium bromide.

Additive (iii)b was tetra-n-pentylammonium bromide.

Additive (xii) was a "butylated polyvinyl pyrrolidone" sold under the Trade Mark "Antaron" P904 by International Speciality Products of Wayne, N.J., USA, which is a water soluble copolymer powder with structural units derived from 90% N-vinyl pyrrolidone and 10% butylene and prepared by polymerisation with t-butylperoxide; it is believed to be a graft copolymer of poly vinyl pyrrolidone (K30)
and butylene, with the butylene structural units in the pyrrolidone ring and/or part of the hydrocarbon backbone and/or pendant thereon. The chemical has a weight average molecular weight of about 16000.

Additive (xiii) was a vinyl pyrrolidone copolymer sold under the Trade Mark "Antaron" VC 713 by International Speciality Products of Wayne, N.J., USA, which is a powder of a copolymer which is a terpolymer with structural units from N-vinyl pyrrolidone, N-vinyl-omega caprolactam and dimethylaminoethyl methacrylate.

Example 1

\[ n\text{-Pentyl-tris[2-(2-methoxyethoxy)ethyl]ammonium bromide.} \]

\[ \text{Tris[2-(2-methoxyethoxy)ethyl]amine (16.2g, 0.05 mole) and} \]

1-bromopentane (17.0g, 0.11 mole) were dissolved in acetonitrile (50ml) and heated under reflux (about 80°C) for 42 hours. The solvent was evaporated with a rotary film evaporator to leave a crude product, which was extracted with diethyl ether (50ml) to remove any unreacted amine and from bromopentane and give 2 phases. The lower oily layer was separated from the upper ether layer, and was then evaporated to leave an oily product (13.8g). Proton and \(^{13}\)Cnmr on the oily product supported an analysis of it as about 95% of n-pentyl tris[2-(2-methoxyethoxy)ethyl]ammonium bromide and about 5% of tris[2-(2-methoxyethoxy)ethyl ammonium bromide.

Example 2

\[ n\text{-Dodecyl-[tris(hydroxymethyl)methyl]dihydrogen ammonium bromide.} \]

\[ \text{Tris(hydroxymethyl)amino methane (12.1g, 0.1 mole) and 1-}

bromododecane (24 9g, 0.1 mole) were dissolved in acetonitrile (40ml) and the solution obtained heated under reflux (about 80°C) for 70 hours. On cooling, the slurry obtained was filtered to leave an insoluble solid which was washed with diethyl ether and dried to give a crude product (Yield 25.8g of about 70% purity). Crude product (10g) was recrystallised from 10% vol hydrochloric acid (220ml) to give a white, crystalline product whose proton nmr spectrum was consistent with dodecyl-[tris(hydroxymethyl)methyl] dihydrogen ammonium bromide.

Examples 3-9

The formulations were made up and added to the water so it contained the Additives below in amounts (in ppm relating to total water present). The results (averaged over several repeat experiments) were as follows:

35
### Additive Amount (ppm)

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<th>Ex.</th>
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<th>(i)</th>
<th>(xiv)</th>
<th>(xxi)</th>
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<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>22</td>
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</table>

In Ex. C and 9, the 2% propane 98% methane gas of the other Examples was replaced by 100% methane.

In Ex.5 and 8, the experiments were done with 100ml heptane and 100ml water in the cell.

### Example 10-13

The processes of Ex.3-8 were repeated with the following formulations and results:

<table>
<thead>
<tr>
<th>Ex.</th>
<th>(iii)</th>
<th>(xii)</th>
<th>(xiii)</th>
<th>(xiv)</th>
<th>(xxi)</th>
<th>Total</th>
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<td>4040</td>
<td>730</td>
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Claims

1. A blend of at least two of an additive (xx) which is an ammonium salt containing at least one oxygen atom of general formula $[R_{20}^+ \cdot N\cdot R_{21}\cdot R_{22}\cdot R_{23}]^- \cdot X^{1/v}$ wherein $R_{20}$ is an organic group and each of $R_{21}$, $R_{22}$ and $R_{23}$, which may be the same or different, represents a hydrogen atom or an organic group containing at least one oxygen atom in a hydroxyl or an ether group, with the proviso that at least one of $R_{21}$, $R_{22}$ and $R_{23}$ contains at least one oxygen atom, and $X$ is an anion of valency $v$, where $v$ is an integer of 1-4, additive (xxi) which is a polyamino acid or salt thereof which has structural units derived from at least one amino acid, at least 50% of which units have at least two carboxylic acid groups, additive (i) which is a polymer of (a) an ethylenically unsaturated N-heterocyclic carbonyl compound and optionally (b) a different ethylenically unsaturated N-heterocyclic carbonyl compound with 5-7 ring atoms in the heteroring, the numbers of heteroring atoms in (a) and (b) differing by at least one, additive (ii) which is a corrosion inhibitor, additive (iii) which is a salt of formula (SEE SPEC page 5 lines 20-26), additive (ix) which is at least one water soluble polymer of a polar ethylenically unsaturated compound, additive (x) which is a hydrophilic colloid, additive (xii) which is an aliphatic (N-heterocyclic carbonyl) polymer with a hydrocarbon backbone, additive (xiii) which is a copolymer of (a) least one ethylenically unsaturated N-heterocyclic ring compound with at least one of b) a different ethylenically unsaturated N-heterocyclic ring compound and c) a polar ethylenically aliphatic unsaturated compound, different from said N-heterocyclic compounds, said copolymer (xiii) being different from additive (i), and additive (xiv) which is an anti-foaming agent with the proviso that at least one of additive (xx) and additive (xxi) is present.

2. An ammonium salt containing at least one oxygen atom of general formula
[R_{20}^+ N R_{21} R_{22} R_{23}]^+X \nu \text{ wherein } R_{20} \text{ is an organic group and each of } R_{21}, \ R_{22} \text{ and } R_{23}, \text{ which may be the same or different, represents a hydrogen atom or an organic group containing at least one oxygen atom in a hydroxyl or an ether group, with the proviso that at least one of } R_{21}, R_{22} \text{ and } R_{23} \text{ contains at least one oxygen atom, and } X \text{ is an anion of valency } v \text{, where } v \text{ is an integer of } 1-4, \text{ n}

3. An ammonium salt according to Claim 2 which is a monoalkyl ammonium tris(hydroxyalkyl), a tris(polyalkyleneoxy), a tris(alkoxy polyalkyleneoxy) or a monoalkyl[(tris(hydroxymethyl)]methyl]ammonium salt.

4. A blend according to Claim 1 in which additive (xx) is as defined in Claim 3

5. A blend according to Claim 1 or 4 in which additive (xxi) is polyaspartic acid or salt or precursor thereof

6. A blend according to any one of Claim 1, 4 or 5 in which additive (iii), additive (xii), additive (xiii), additive (xiv) and additive (xxi) are present

7. A blend according to any one of Claim 1, 4 or 5 in which additive (xx).

8. A blend according to any one of Claim 1, 4, 5, 6 or 7 in which, if present, additive (i) is homopolymeric N-vinyl-omega caprolactam, additive (xii) is a butylated polyvinyl pyrrolidone, additive (iii) is tetra-n-butyl ammonium bromide or tetra-n-pentyl ammonium bromide, additive (xiii) is a vinyl pyrrolidone copolymer and additive (xiv) is a polydimethylsiloxane

9. A blend according to any one of Claim 1, 4, 5, 6, 7 or 8 in which the weight ratio of additive (xx) to additive (xxi) is 70:30 to 95:5 or 40:60 to 60:40

10. A blend according to any one of Claim 1, 4, 5, 6, 7 or 8 in which the weight ratio of each, if present, of additives (i), (ii), (iii), (ix), (x), (xii) and (xiii) to additive (xxi) is 75-90 : 25-10 or 90:10 to 99:1

11. A blend according to any one of Claims 1 and 4-10 in which the total additive concentration in water is 50-10,000 ppm.

12. An oil-based drilling mud comprising additive (xx) or additive (xxi) and at least one additive (ii), (iii), (ix), (x), (xii), (xiii) and (xiv) as defined in any one of Claim 1, 4, 5 or 8

13. Use of a blend as claimed in any one of Claim 1, 4, 5 or 8 in the transportation of fluids comprising gas and water.

14. A method for inhibiting or retarding hydrate formation which method comprises adding a blend as claimed in any one of Claim 1, 4, 5 or 8 to a medium susceptible to hydrate formation.
A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E21B3/06 C10L3/00

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)
IPC 6 E21B C10L

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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- Further documents are listed in the continuation of box C.

- Patent family members are listed in annex.

- Special categories of cited documents:
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  - O: document referring to an oral disclosure, use, exhibition or other means
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  - &: document member of the same patent family

Date of the actual completion of the international search: 14 June 1996
Date of mailing of the international search report: 26-06-1996

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Authorized officer
De Herdt, O
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