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Fortsættes ...

DESCRIPTION

[0001] The invention relates to the use of a composition and a process for scavenging hydrogen sulfide from liquids and/or gas by using a synergistic combination of acetals with a reaction product from formaldehyde and amines and a solids suppression agent. The formulations containing the composition have particular applicability in scavenging hydrogen sulfide and/or mercaptans yet at the same time prevent the formation of unwanted emulsions and/or deposition of unwanted byproducts often associated with using chemistries and/or formulations of the prior art.

[0002] The presence of compounds containing a sulfhydryl group (-SH) and particularly of hydrogen sulfide pose challenges in many industries. Their presence can create a significant health, safety and environmental challenge. There are many different types of compounds containing a sulfhydryl group ("sulfhydryl compounds"), with the most commonly encountered molecules including hydrogen sulfide (H_2S), organo-sulfur compounds containing R-SH groups (also called mercaptans), thiocarboxylic acids $RC(O)SH$, dithiocarboxylic acids $RC(S)SH$, and related compounds.

[0003] In the oil and gas industry the H_2S content of crude oil and natural gas in many areas of the world is high enough to present environmental and safety hazards. Hydrogen sulfide is a flammable, corrosive, and highly toxic gas. H_2S is the most reduced form of sulfur and is produced by sulfate reducing bacteria (SRB) that are often found in anaerobic oilfield environments, or caused by thermal cracking and thermochemical sulfate reduction (TSR) by hydrocarbons. As crude oil is produced, it is depressurized and dissolved H_2S is released and can then be transferred to, for example, oil based drilling fluid during the drilling process and this can become a hazard as the drilling fluid is recirculated from the well to the surface. During the production phase of crude oil and natural gas H_2S gas can create a significant asset integrity risk as it is an acid gas and upon dissolving into produced water creates a very corrosive environment. In addition, the presence of H_2S increases the risks of sulfide stress cracking, hydrogen embrittlement and pitting corrosion of some structural materials and requires to be removed in order for fluids and gases to be safely processed.

[0004] The odor of sulfhydryl compounds is also a challenge in, for example, metal working environments, but equally in water treatment processes, either municipal (e.g. waste water treatment) or industrial (e.g. recycling of mining water). SRB are often present in the recirculating fluid systems, and though the bacteria can usually be controlled by the use of biocidal compositions, often control of the biology in the system gets lost which results in the development of hazardous H_2S and/or mercaptans in the system. Furthermore biocides are inefficient at removing H_2S after it forms and only anecdotally scavenge, *via* either oxidation (e.g. sodium hypochlorite application) or due to the release of low levels of aldehyde during their breakdown (e.g. with glutaraldehyde). Sulfhydryl compounds and particularly H_2S can present environmental, toxicity and integrity challenges in gaseous phases in confined spaces,

as for instance in sewage treatment facilities and particularly in shipping and storage containers for moisture sensitive materials that may emit H_2S which can accumulate in the gaseous headspace. It would be desirable to have a scavenger that can reduce the H_2S concentration in such locations.

[0005] Most commonly used sulfhydryl scavengers are based on metals as for example copper, zinc or iron which are converted to insoluble sulfides. A number of alternative, metal free methods have been proposed to scavenge hydrogen sulfide and to control sulfhydryl odors in hydrocarbon containing systems, including:

WO-98/02501 describes the use of bisoxazolidines prepared by the reaction of 1, 2 or 1, 3 amino alcohols containing 3 to 7 carbon atoms with aldehydes containing 4 or fewer carbon atoms, as for example 3,3'-methylenebis-5-methyloxazolidine. The relative oil and water solubility of these products can be controlled through the choice of starting materials. These bisoxazolidines react with sulfhydryl compounds present in oil and gas streams to neutralize and therefore scavenge them.

[0006] US-8329063 teaches a composition with reduced formaldehyde and amine emission which may be used as a preservative, wherein said composition comprises:

1. a) at least one N-formal;
2. b) at least one emission reducing additive, wherein said reducing additive comprises at least one member selected from the group consisting of:
 1. 1) urea;
 2. 2) urea derivatives;
 3. 3) amino acids;
 4. 4) guanidine; and
 5. 5) guandine derivatives; and
3. c) monoethylene glycol.

[0007] US-5728263 teaches the use of dialdehydes and acetals thereof for inhibiting decomposition of peroxide in the production and the treatment of recycled fiber pulp and other fiber pulp.

[0008] US-3880784 teaches stable solutions of diisocyanate polyaddition products in a solvent mixture containing:

1. (a) inert organic solvents,
2. (b) primary and/or secondary alcohols and
3. (c) semiacetals of formaldehyde and the process of preparing such solutions.

[0009] US-5347004 teaches the use of reaction products of alkoxyalkylene amine, optionally in

admixture with ammonia and/or alkylamines with aldehydes to remove H₂S from gas streams which are sparged into water solutions of the reaction products.

[0010] WO-2014/031537 teaches the use of an aldehyde releasing compound, preferably hydantoins, to remove sulfhydryl compounds from hydrocarbon fluids.

[0011] US-3928211 describes the use of inorganic zinc salts (most preferably zinc carbonate) preferably dispersed into aqueous or non-aqueous oil well drilling fluids with an organic dispersant such as lignin containing materials for scavenging hydrogen sulfide in aqueous drilling fluids.

[0012] WO-2002/051968 teaches a process for reducing the level of hydrogen sulfide in a liquid or gas by treatment of the liquid or gas with an H₂S-scavenger product derivable from the reaction of a carbonyl group-containing compound with an alcohol, thiol, amide, thioamide, urea or thiourea. The carbonyl group-containing compound is preferably formaldehyde, and preferably the product is derivable by reaction of formaldehyde with an amine-free alcohol or urea selected from ethylene glycol, propylene glycol, glycerol, diethylene glycol, triethylene glycol, ethyl alcohol, n-butanol, a sugar, a low molecular weight polyvinyl alcohol, castor oil fatty acid and urea. More especially, the scavenger product is used with an amine, especially monoethanolamine or monoethanolamine triazine.

[0013] US-4978512 teaches a method of reducing H₂S levels, the method comprising bringing the H₂S containing medium into contact with inter alia acetals and bisoxazolidines.

[0014] The object of this invention is to provide compositions which can be used for scavenging of sulfhydryl compounds in crude oil, gas production, water production, water injection and combinations thereof, preferably, but not limited to, H₂S and/or mercaptans. The compositions of the invention should be notable for improved safety and performance compared to the formulations and chemistries of the prior art, i.e. they should contain low amounts of toxic substances like formaldehyde even after prolonged storage, have a higher scavenging efficiency and especially for the treatment of gases as for example of natural gas assure an efficient scavenging of sulfhydryl compounds within a short contact time. Furthermore it is desirable to have a scavenger that does not produce unwanted solid by-products and/or form emulsions that can inadvertently contaminate the very systems they are treating.

[0015] Surprisingly it has been found that a composition comprising at least one reaction product between a monohydric alcohol and an aldehyde or ketone and at least one reaction product of a polyhydric alcohol and an aldehyde or ketone shows improved capability in scavenging sulfhydryl compounds in comparison to reaction products of the individual alcohols. Such composition allows i) for a lower dosage rate of scavenger to obtain the same level of residual amount of sulfhydryl compound and/or ii) for a lower level of residual amount of sulfhydryl compound with the same dosage rate of scavenger. Furthermore, in combination

with at least one reaction product from formaldehyde and an amine (hereinafter also referred to as "synergist") the kinetics of scavenging H_2S and/or mercaptans provided by the reaction products of a monohydric alcohol and a polyhydric alcohol with an aldehyde and/or ketone can be significantly accelerated. Alternatively or in addition to the first two components of the composition, the admixture of a solids suppression agent as further synergistic additive facilitates the removal of sulfhydryl reaction products in continuously operated scavenging processes. Furthermore such admixture extends the gas breakthrough time of sulfhydryl compounds in a contact tower containing the reaction product of a monohydric alcohol and a polyhydric alcohol with an aldehyde and/or ketone.

[0016] The use of the synergist and/or the further synergist of the invention enables the mixed hemiacetals and acetals to react much more efficiently with sulfhydryl compounds and especially with H_2S . The mechanism believed to be involved in this reaction, but should not be considered to be limiting to the invention in any way, occurs due to the likelihood that the synergist component reacts preferentially with H_2S forming an intermediate reaction complex which then in turn reacts with a molecule of hemiacetal respectively acetal reforming a molecule of synergist and liberation of the corresponding alcohol present in the acetal. After the H_2S scavenging process the residual synergist then works as a corrosion inhibitor, protecting the integrity of the pipelines and equipment in which it has been applied.

[0017] Within the scope of this application the expressions "hemiacetal" and "acetal" encompass the reaction products of an alcohol with either an aldehyde or a ketone, i. e. they include hemiketals respectively ketals when using a ketone instead of an aldehyde in the reaction with an monohydric and/or polyhydric alcohol. The expression "(hemi-)acetals" encompasses hemiacetals, acetals and their mixtures which are often formed during reaction of alcohols and carbonyl compounds.

[0018] In a first aspect of the invention, there is provided the use of a composition comprising

1. I. at least one reaction product between a nitrogen-free monohydric alcohol and an aldehyde or ketone, and
2. II. at least one reaction product between a nitrogen-free polyhydric alcohol and an aldehyde or ketone, as a scavenger for sulfhydryl compounds for application in oilfield operations and process systems.

[0019] In a second aspect of the invention there is provided the use of a composition comprising

1. I. at least one reaction product between a nitrogen-free monohydric alcohol and an aldehyde or ketone, and
2. II. at least one reaction product between a nitrogen-free polyhydric alcohol and an aldehyde or ketone, and

3. III. at least one reaction product from formaldehyde and ammonia and/or an amine, selected from the group consisting of primary alkyl amines having 1 to 10 carbon atoms and primary hydroxy alkyl amines having 2 to 10 carbon atoms, as a scavenger for sulfhydryl compounds for application in oilfield operations and process systems.

[0020] In a third aspect of the invention there is provided the use of a composition comprising

1. I. at least one reaction product between a nitrogen-free monohydric alcohol and an aldehyde or ketone, and
2. II. at least one reaction product between a nitrogen-free polyhydric alcohol and an aldehyde or ketone, and
3. III. at least one reaction product from formaldehyde and ammonia and/or an amine, selected from the group consisting of primary alkyl amines having 1 to 10 carbon atoms and primary hydroxy alkyl amines having 2 to 10 carbon atoms, and
4. IV. at least one inorganic or organic alkaline compound that functions as a solids suppression agent, as a scavenger for sulfhydryl compounds for application in oilfield operations and process systems.

[0021] In a fourth aspect of the invention, there is provided a process for scavenging sulfhydryl compounds in oilfield operations and process systems, the process comprising adding to a system susceptible to liberation of sulfhydryl compounds a composition as described in the first, second or third aspect of the invention.

[0022] In preferred embodiments of the invention, at least one demulsifier (V) and/or corrosion inhibitor (VI) is present in any aspect of the invention.

Group I

[0023] The group I compound is the reaction product of a monohydric alcohol and an aldehyde or ketone. The monohydric alcohol does not contain nitrogen.

[0024] Monohydric alcohols as starting materials are alkyl, aryl and arylalkyl alcohols containing one hydroxy group and 1 to 15 carbon atoms, more preferably 1 to 10 carbon atoms and especially 2 to 5 carbon atoms as for example 1 to 5, 2 to 15 or 2 to 10 carbon atoms. The hydroxyl group of preferred alcohols is bound to an aliphatic, alicyclic and/or aromatic moiety, preferably to an aliphatic, alicyclic and/or aromatic hydrocarbon moiety, and more especially to an aliphatic or cycloaliphatic moiety. The aliphatic and cycloaliphatic moieties may be saturated or unsaturated, preferably they are saturated. Aliphatic moieties with 3 or more carbon atoms may be linear or branched. More especially the monohydric alcohol is aliphatic. In particular the alcohol is an alkyl alcohol. Examples for preferred alcohols

are methanol, ethanol, propanol, iso-propanol, n-butanol, iso-butanol, tert-butanol and the various isomers of pentanol, hexanol, heptanol and octanol as for example 2-ethyl hexanol and their mixtures. Especially preferred are methanol and ethanol.

[0025] Preferred aldehydes or ketones as starting materials contain one or more carbonyl groups, more preferably one or two carbonyl groups and especially one carbonyl group. Furthermore, aldehydes and ketones contain 1 to 10 carbon atoms, more preferably 1 to 7, and especially 1 to 4 carbon atoms. In preferred aldehydes the carbonyl group carries one and in preferred ketones two aliphatic, alicyclic and/or aromatic substituents, more preferably aliphatic, alicyclic and/or aromatic hydrocarbon substituents. Preferred aliphatic and cycloaliphatic substituents may be saturated or unsaturated, most preferably they are saturated. In ketones both substituents may be the same or different.

[0026] In a preferred embodiment the carbonyl compound is an aldehyde, more preferably a mono- or di-aldehyde, and especially formaldehyde. It should be understood that the terms "aldehyde" and "formaldehyde" include precursors like e.g. para-formaldehyde, formalin, and other chemical forms from which the basic structure HCHO can be released or set free during the reaction with an alcohol. Other suitable aldehydes include, for example, acetaldehyde, propionaldehyde, butyraldehyde, glutaraldehyde and glyoxal. Suitable ketones include, for example, acetone, methyl ethyl ketone, diethylketone, methyl isopropyl ketone, hexanones and heptanones.

[0027] Mixtures of two or more carbonyl compounds, for example two or more of the aldehydes mentioned above, e.g. formaldehyde and one or more other aldehydes, may be used if desired.

[0028] In the reaction between monohydric alcohol and aldehyde and/or ketone part or all of the alcohols may be converted to hemiacetals and/or acetals. In a preferred embodiment, the reaction product is a hemiacetal. In a preferred embodiment at least 50 mol-% of the alcohol, more preferably 60 to 99 mol-% of the alcohol, especially 65 to 95 mol-% of the alcohol and especially preferred 70 to 90 mol-% of the alcohol as for example more than 60 mol-%, more than 65 mol-%, more than 70 mol-%, % of the alcohol or 50 to 99 mol-%, 50 to 95 mol-%, 50 to 90 mol-%, 60 to 95 %, 60 to 90 mol-%, 65 to 99 mol-%, 65 to 90 mol-%, 70 to 99 mol-% or 70 to 95 mol-% of the alcohol are converted to hemiacetals and/or acetals. In case the degree of conversion is low some unreacted monohydric alcohol remains in the composition. The presence of residual alcohol in the reaction mixture has proven to be advantageous as upon its reaction with sulfhydryl compounds often the formation of solid precipitate gets reduced. Furthermore, remaining alcohol will act as a solvent.

Group II

[0029] The group II compound is the reaction product of a polyhydric alcohol and an aldehyde or ketone. The polyhydric alcohol does not contain nitrogen.

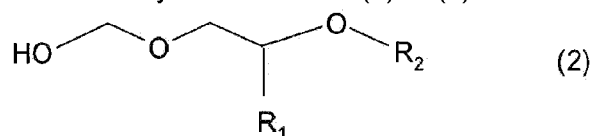
[0030] Polyhydric alcohols as starting materials contain 2 to 20 carbon atoms and 2 to 6, more preferably 3 to 6 hydroxy groups. Preferred polyhydric alcohols contain 3 to 10 carbons atoms 3 to 20 carbon atoms. Preferably they are aliphatic. Examples for preferred polyhydric alcohols are ethylene glycol, propylene glycol, butylene glycol, pentanediol, neopentyl glycol, hexanediol, glycerol, pentaerythritol, diethylene glycol, triethylene glycol, an oligomer of glycerol with 2 or 3 repeating units, a sugar molecule (i.e. a monosaccharide or disaccharide compound), or a polyvinyl alcohol of low molecular weight such that the reaction product with the carbonyl starting material remains a liquid. It is preferred that the number of hydroxyl groups in the polyhydric alcohol is lower or at most equal to the number of carbon atoms. Most preferred polyols are ethylene glycol and glycerol.

[0031] Preferred aldehydes and ketones as starting materials for the group II compounds are the aldehydes and ketones that have already been described above with respect to Group I. Most preferred aldehyde for group II compounds is formaldehyde. The aldehyde or ketone used for reaction with the polyhydric alcohol may be the same as the one used for the monohydric alcohol, or it may be a different one.

[0032] In the reaction between polyhydric alcohol and aldehyde and/or ketone part or all of the hydroxyl groups may be converted to hemiacetals and/or acetals. In a preferred embodiment at least 50 mol-% of the hydroxyl groups, more preferably 60 to 99 mol-% of the hydroxyl groups, especially 65 to 95 mol-% of the hydroxyl groups and especially preferred 70 to 90 mol-% of the hydroxyl groups as for example more than 60 mol-%, more than 65 mol-%, more than 70 mol-%, % of the alcohol or 50 to 99 mol-%, 50 to 95 mol-%, 50 to 90 mol-%, 60 to 95 %, 60 to 90 mol-%, 65 to 99 mol-%, 65 to 90 mol-%, 70 to 99 mol-% or 70 to 95 mol-% of the hydroxyl groups are converted to hemiacetals and/or acetals. In case the degree of conversion is low some unreacted polyhydric alcohol remains in the composition. The presence of residual hydroxyl groups in the reaction mixture has proven to be advantageous as upon its reaction with sulfhydryl compounds the formation of solid precipitate gets reduced.

[0033] In a particularly preferred embodiment the reaction product is predominantly a hemiacetal derived from the polyhydric alcohol. Especially preferred are reaction products wherein the ratio between hemiacetals and acetals on a molar basis is between 50:1 and 1:10 and especially between 20:1 and 1:2 as for example between 50:1 and 1:2 or between 20:1 and 1:10.

[0034] Preferred polyhydric hemiacetal compounds that can be used as the scavenger are described by the structures (2) to (5) below:



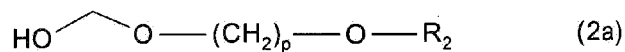
wherein

R₁

is H or C₁ to C₈ alkyl, and

R₂

is H or CH₂OH.



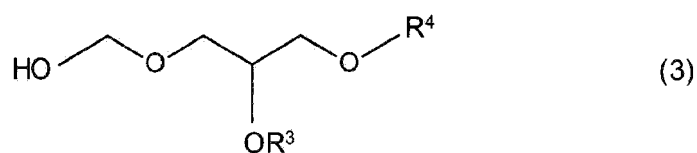
wherein

p

is a number from 2 to 10, and

R₂

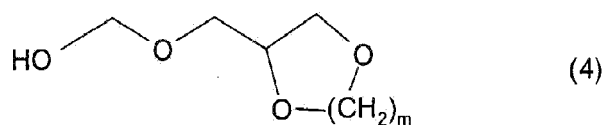
is H or CH₂OH



wherein

R₃ and R₄

independently are H or CH₂OH

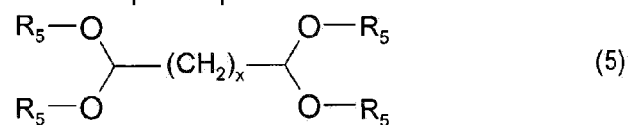


wherein

m

is 1 to 10, preferably 1 or 2

[0035] The most preferred structures are the ones derivable from either glycerol or ethylene glycol. These correspond to the formulae (3) and (4), or formula (2) wherein R₁ is H. In another specific preferred embodiment the hemiacetal can have the structure below



wherein

R₅

is H, CH₃, (CH₂)_zCH₃, with the proviso that not all of R₅ are hydrogen,

z

is 1 to 10, and

x

is 1 to 5.

[0036] Reactions of aldehydes and ketones with alcohols are described in the literature. "Formaldehyde", p 265, Joseph Frederic Walker, reprint 1975, Robert E. Krieger Publishing Company Inc. discloses that hemiacetals are obtained when formaldehyde and alcohols are brought together under neutral or alkaline conditions, and that they form readily in the case of primary and secondary alcohols.

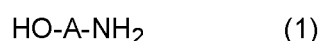
[0037] The synthesis of compounds of group I and group II may be accomplished in separate reactions. Preferably it is accomplished in a simultaneous reaction using a one pot reaction by charging a mixture of monohydric alcohol and polyhydric alcohol and reacting this mixture with the aldehyde and/or ketone. A one-pot reaction is especially preferred when the aldehyde used for the reaction with the monohydric alcohol is the same as the aldehyde used for the reaction with the polyhydric alcohol.

[0038] In the synthesis of compounds of group I and group II the molar ratio of hydroxyl groups to carbonyl groups is preferably between 20:1 and 1:5 and more preferably between 10:1 and 1:2 and especially between 2:1 and 1:1 as for example between 20:1 and 1:2 or between 20:1 and 1:1 or between 10:1 and 1:5 or between 10:1 and 1:1 or between 2:1 and 1:5 or between 2:1 and 1:2.

Group III

[0039] The group III component is optional. The group III compound is the reaction product from formaldehyde with ammonia and/or an amine, the amine being selected from the group consisting of primary alkyl amines having 1 to 10 carbon atoms and primary hydroxy alkyl amines having 2 to 10 carbon atoms. This group comprises the synergist component of the inventive composition.

[0040] Preferred primary amines comprise 1 to 4 carbon atoms, preferred primary hydroxy amines 2 to 4 carbon atoms. Especially preferred primary hydroxy amines correspond to the formula (1)



wherein A is a linear or branched alkylene group with 2 to 4 carbon atoms.

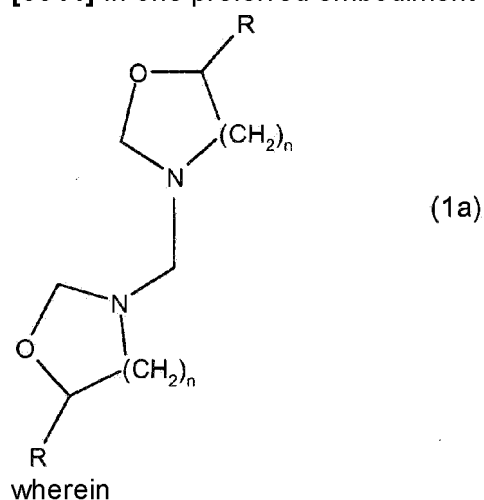
[0041] Examples of nitrogen containing compounds suitable for the present invention include,

but are not limited to: ammonia, methylamine, ethylamine, propylamine, isopropyl amine, monoethanolamine, 1-amino-2-propanol, 3-amino-1-propanol, 2-amino-1-butanol, 3-amino-1-butanol, 3-amino-1-butanol, 2-ethoxypropylamine, 3-ethoxypropylamine, 1-methoxyisopropylamine and 2-methoxyethylamine.

[0042] The nitrogen containing compound and formaldehyde may be reacted in any molar ratio with a preferred ratio being from 1 mole aldehyde to 10 moles nitrogen containing compound to 10 moles aldehyde to 1 mole nitrogen containing compound, a more preferred ratio being from 1 mole aldehyde to 5 moles nitrogen containing compound to 5 moles aldehyde to 1 mole nitrogen containing compound, an even more preferred ratio being 1 mole aldehyde to 3 moles nitrogen containing compound to 3 moles aldehyde to 1 mole nitrogen containing compound and a most preferred ratio being 1 mole aldehyde to 1 mole nitrogen containing compound.

[0043] The structure of the aminal formed from the reaction of formaldehyde and nitrogen containing compound is dependent upon the selected nitrogen containing compound and the selected molar ratio between formaldehyde and nitrogen compound, as is self-evident to those of ordinary skill in the art. Similarly, mixtures of the above nitrogen containing compounds may also be reacted in order to form singular, or mixtures of various aminals as is also evident to one of ordinary skill in the art.

[0044] In one preferred embodiment the reaction product corresponds to formula (1a)

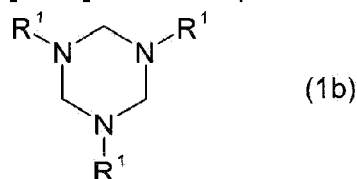


R
is H or methyl, and
n
is 1 or 2.

[0045] In an especially preferred embodiment R is CH₃. In another especially preferred embodiment, n is 1. In a particularly preferred embodiment n is 1 and R is CH₃. The name of

this compound is 3,3'-methylenebis-5-methyl-oxazolidine (MBO).

[0046] In another preferred embodiment the reaction product corresponds to formula (1b)



wherein each R¹ is C₁ to C₄ alkyl or C₂ to C₄ hydroxy alkyl. Examples for especially preferred compounds are hexahydro-1,3,5-trimethyl-s-triazine, hexahydro-1,3,5-triethyl-s-triazine, hexahydro-1,3,5-tris(hydroxymethyl)-s-triazine and hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine.

[0047] Mixtures of different reaction products of structures 1a and 1b are equally suited. The substituents R and R¹ may be the same or different.

Group IV

[0048] The group IV component is optional. The group IV compound is an inorganic or organic alkaline compound. This group comprises the solids suppression agent.

[0049] The solid usually formed by the reaction of group I and group II compounds with hydrogen sulfide is 1,3,5-trithiane. Addition of an alkaline compound to the compounds of groups I and II prevents or at least retards the formation of the poorly soluble 1,3,5-trithiane upon reaction with sulfhydryl compounds. Without being bound to this theory it is believed that different intermediates as for example polyoxymethylenesulfide oligomers are formed and stabilized by the presence of the alkaline compound of group IV. By preventing the formation of solids the scavenging composition remains homogeneous and especially in a contact tower application allows for more efficient and up to quantitative use of the (hemi-)acetals of group I and II compounds and thereby reduces the amount of chemicals required. This may result in an extended gas breakthrough time in such scavenging applications. Additionally, in direct injection applications for continuous scavenging of sulfhydryl compounds from e.g. natural gas streams the removal of the liquid reaction products is much easier than removal of solids and it is not prone to blockage of tubings.

[0050] Furthermore, in the presence of an alkaline compound of group IV the stability of compounds I and II is increased and gassing of formaldehyde is reduced or even prevented. This leads to a reduced level of free formaldehyde in the space above the composition and thereby improves the safety of the personnel handling the inventive composition.

[0051] Preferably, the compound of group IV is soluble in, or miscible with the mixture of compounds of groups I and II. In a further preferred embodiment the compound of group IV is soluble in, or miscible with the formulation of the mixture of compounds of groups I and II in the

presence of an aqueous solvent.

[0052] In a preferred embodiment, the alkaline compound is selected from the group consisting of

IV(a). alkaline metal salts or alkaline earth metal salts,

IV(b). ammonia; alkyl, aryl or alkylaryl amines,

IV(c). hydroxy alkyl, hydroxyl aryl or hydroxy alkylaryl amines,

IV(d). multifunctional amines, and

IV(e). mixtures of compounds of groups IV(a) to IV(c).

[0053] In an aryl amine, the N atom is bonded to the aromatic system. In an alkyl aryl amine, the N atom may be bonded to either the aromatic system or the alkyl group.

[0054] Preferred cations of the alkaline metal and alkaline earth metal salts IV(a) are derived from lithium, sodium, potassium, rubidium, beryllium, magnesium, calcium and strontium with sodium, potassium and calcium being especially preferred. Preferred anions are hydroxyl and carbonate groups with hydroxyl being especially preferred. Examples for preferred alkali or alkaline earth metal salts LiOH , NaOH , KOH , $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Be}(\text{OH})_2$, Na_2CO_3 , K_2CO_3 , NaHCO_3 , KHCO_3 , BeCO_3 , MgCO_3 , CaCO_3 , $\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{HCO}_3)_2$ and their mixtures. Especially preferred alkali and alkaline earth metal salts of group IVa are NaOH , KOH , $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$.

[0055] The amines of group IV(b) may be primary, secondary or tertiary amines. Preferred amines have up to 20 carbon atoms, more preferably between 1 and 10 and especially between 2 and 4 carbon atoms as for example between 1 and 20, between 1 and 4, between 2 and 20 or between 2 and 10 carbon atoms. Preferred hydrocarbyl residues are alkyl, aryl and alkylaryl residues, with alkyl residues being particularly preferred. Especially preferred amines are alkyl amines with 1 to 4 carbon atoms per alkyl residue. Examples for especially preferred amines are methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, propylamine, isopropylamine and butylamine.

[0056] The hydroxy amine of group IV(c) may be a primary, secondary or tertiary amine. It may contain one, two or three hydroxy groups. In a preferred embodiment each hydrocarbyl substituent of the nitrogen is substituted by not more than one hydroxy group. Preferred amines have up to 20 carbon atoms, more preferably between 1 and 10 and especially between 2 and 4 carbon atoms as for example between 1 and 20, between 1 and 4, between 2 and 20 or between 2 and 10 carbon atoms. Preferred hydrocarbyl residues are alkyl, aryl and alkylaryl residues, with alkyl residues being particularly preferred. Especially preferred hydroxy amines are hydroxyalkyl amines with 1 to 4 carbon atoms per alkyl residue. Examples for

especially preferred hydroxy amines of group IV(c) are monoethanolamine, diethanolamine, 1-amino-2-propanol, 3-amino-1-propanol, 2-amino-1-butanol, 3-amino-1-butanol, 3-amino-1-butanol, 2-ethoxypropylamine, 3-ethoxypropylamine, 1-methoxyisopropylamine, 2-methoxyethylamine, 2-(2-aminoethoxy)ethanol, dimethylethanolamine, N-methyldiethanolamine and monomethylethanolamine.

[0057] Preferred multifunctional amines of group IV(d) contain, besides an amino group, at least one further functional group selected from the group consisting of amino groups, ether groups and acid groups or an ester, amide or salt thereof. Preferred multifunctional amines have up to 50 carbon atoms, more preferably between 1 and 20 and especially between 2 and 10 carbon atoms as for example between 1 and 50, between 1 and 10, between 2 and 50 or between 2 and 20 carbon atoms. The hydrocarbon chains may be linear, branched and/or cyclic. In a preferred embodiment they contain 1 to 10 and especially 2 to 5 as for example 1 to 5 further amino groups and/or ether groups. Preferably the amino- and/or ether groups are separated by at least two carbon atoms. Examples for especially preferred multifunctional amines of group IV(d) are ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, poly(ethylene imine), propylene diamine, dipropylenetriamine, N,N-dimethyldipropylenetriamine, aminoethylenepiperazine, aminoethylethanolamine, tallow fatty propylene diamine ethoxylated with 2 to 20 moles ethylene oxide, oleyl amine ethoxylated with 2 to 20 mole ethylene oxide, morpholine and piperazine.

[0058] In a further preferred embodiment the multifunctional amines of group IV(d) contain, besides an amino group, an acid group or an ester, amide or salt thereof. Preferred acid groups are sulfonic acids, phosphoric acids and carboxylic acids. Especially preferred multifunctional amines carrying a carboxylic acid group are amino acids. Preferred amino acids include proteinogenic and non-proteinogenic amino acids. The amino group and the carboxylic acid group may be located at the same or at different carbon atoms. Carboxylic acid groups and other acidic groups are especially preferred in their neutralized form, e.g. as alkaline or earth alkaline salts. Especially preferred amino acids contain further functional groups including, hydroxyl, carboxyl, amide, ether, guanidino, hydroxyphenyl, imidazolyl and/or further amine groups. Examples of preferred multifunctional amines carrying an acid group are glycine, alanine, leucine, isoleucine, proline, serine, threonine, asparagine, glutamine, phenylalanine, tryptophan, tyrosine, valine, aspartic acid, glutamic acid, methionine, sarcosine and taurine and their carboxylate salts with sodium and/or potassium. Especially preferred amino acids are glycine, lysine, histidine and arginine.

[0059] When mixtures IV(d) of alkaline compounds of the groups IV(a) to IV(c) are used, they may comprise 2 or more, preferably 2 to 10 and especially 3 to 5 as for example two, three, four or five different components selected from the groups IV(a) to IV(c). The portion of each individual compound in the mixture of the compounds of groups IV(a) to IV(c) is preferably between 5 and 95 wt.-%, more preferably between 10 and 90 wt.-% and especially between 20 and 80 wt.-% as for example between 5 and 90 wt.-%, between 5 and 80 wt.-%, between 10 and 95 wt.-%, between 10 and 80 wt.-%, between 20 and 95 wt.-% or between 20 and 90 wt.-%.

C_1 to C_{18} alkyl

k

a number from 1 to 200

m

a number from 1 to 100 is.

[0063] In a preferred embodiment R_{10} is an ethylene or a propylene group. R_{10} may represent mixtures of different C_2 to C_4 alkylene groups, preferably ethylene and propylene groups.

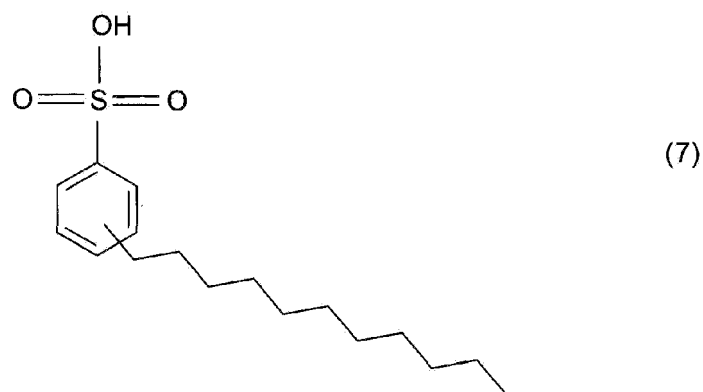
[0064] In another preferred embodiment, R_{11} is a C_4 to C_{12} alkyl group, more preferably a tertiary butyl group or an iso-nonyl group.

[0065] In formula (6), R_{10} , R_{11} and k may be the same in each of the repeating units, or they may differ from unit to unit.

[0066] In another preferred embodiment k is a number from 2 to 20.

[0067] In another preferred embodiment m is a number from 3 to 20.

[0068] In another specific preferred embodiment the emulsion breaker is an alkylbenzenesulfonic as for example dodecylbenzenesulfonic acid (7) or its salt with an alkaline metal, ammonia or a primary, secondary or tertiary amine as for example methylamine, ethylamine, propylamine, diethylamine, dimethylamine, trimethylamine, ethanolamine, diethanolamine or triethanolamine.



[0069] In another preferred embodiment, the demulsifier is a mixture of at least one compound of formula (6) and an alkylbenzene sulfonic acid (7) or its salt. Such mixture preferably contains (6) and sulfonic acid (7), respectively its salt, in a weight ratio of from 5:1 to 1:5, more preferably in a weight ratio of from 3:1 to 1:3.

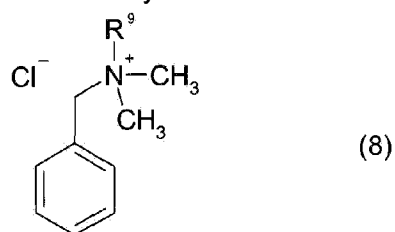
[0070] The polymeric nonionic surfactant may be added to the further components of the

inventive composition neat or preferably dissolved or suspended in a solvent. Any solvent suitable for dissolving or suspending a polymeric nonionic surfactant may be used. Examples of suitable solvents include water, ethylene glycol, propylene glycol, butylene glycol, oligoethylene glycols, oligopropylene glycols, ethers including glycol ethers like methoxyethane, dimethoxyethane and butoxyethanol, alcohols, toluene, xylene, aromatic naphtha, or any combination thereof. The alcohol may include any alcohol suitable for use with oil recovery and for dissolving the polymeric nonionic surfactant and is preferably selected from the group consisting of methanol, ethanol, propanol, isopropyl alcohol, butanol, 2-ethyl hexanol or any combination thereof.

Group VI

[0071] The group VI component is optional. This group comprises corrosion inhibitors and serves to add corrosion inhibition functionality to the inventive composition. The addition of a corrosion inhibitor may not be required because the synergist of group III provides sufficient corrosion inhibition to protect the integrity of the whole asset. However, often addition of a further corrosion inhibitor is advisable to reduce the overall corrosivity, protecting the tubulars and production equipment from corrosion caused by oilfield fluids and gases into which the instant invention is deployed.

[0072] A preferred embodiment of the current invention is to use alkyl dimethyl benzyl ammonium chloride according to formula (8) as a corrosion inhibitor that also provides functionality as an interfacial tension reducer.



wherein R⁹ is C₈ to C₁₈ alkyl.

[0073] The composition may additionally contain biocides, for example, formaldehyde or glutaraldehyde, water dispersants such as polyacrylamide dispersants, oxygen scavengers, antifoams such as acetylenic diols, silicones or polyethoxylated antifoams, and/or flocculants. Preferably their content is less than 10 wt.-% and especially less than 5 wt.-% relative to the components of the groups I to VI.

[0074] In a preferred embodiment, the composition comprises 5 to 60 wt.-% of the reaction product of the monohydric alcohol described above in group I, preferably between 10 and 50 wt.-% and especially between 15 and 40 wt.-% as for example between 5 and 50 wt.-% or between 5 and 40 wt.-% or between 10 and 60 wt.-% or between 10 and 40 wt.-% or between 15 and 60 wt.-% or between 15 and 50 wt.-%.

[0075] In a preferred embodiment, the composition comprises 10 to 90 wt.-% of the reaction product of the polyhydric alcohol described above in group II, preferably between 20 and 80 wt.-% and especially between 25 and 75 wt.-% as for example between 10 and 80 wt.-% or between 10 and 75 wt.-% or between 20 and 90 wt.-% or between 20 and 75 wt.-% or between 25 and 90 wt.-% or between 25 and 80 wt.-%.

[0076] The molar ratio between the reaction product of the monohydric alcohol and an aldehyde or ketone (group I) and the reaction product of the polyhydric alcohol and an aldehyde or ketone (group II) is preferably between 20:1 and 1:20, preferably between 10:1 and 1:10 and especially between 5:1 and 1:5 as for example between 20:1 and 1:10, between 20:1 and 1:5, between 10:1 and 1:20, between 10:1 and 1:5, between 5:1 and 1:20 or between 5:1 and 1:10.

[0077] In a preferred embodiment, the composition comprises 0.1 to 15 wt.-% of the synergist described above in Group III, preferably between 0.5 and 10 wt.-% and especially between 1 and 8 wt.-% as for example between 0.1 and 10 wt.-% or between 0.1 and 8 wt.-% or between 0.5 and 15 wt.-% or between 0.5 and 8 wt.-% or between 1 and 15 wt.-% or between 1 and 10 wt.-%.

[0078] In a preferred embodiment, the composition comprises 1 to 25 wt.-% of at least one solids suppression agent described above in group IV, preferably between 5 and 20 wt.-% and especially between 7 and 18 wt.-%, as for example between 1 and 20 wt.-% or between 1 and 18 wt.-% or between 5 and 25 wt.-% or between 5 and 18 wt.-% or between 7 and 25 wt.-% or between 7 and 20 wt.-%.

[0079] In a preferred embodiment, the composition comprises 0.1 to 10 wt.-% of at least one emulsion breaker described above in group V, preferably between 0.5 and 5 wt.-%.

[0080] In a preferred embodiment, the composition comprises 0.1 to 10 wt.-% of the corrosion inhibitor described above in group VI, preferably between 0.2 and 5 wt.-%.

[0081] The preferred portions of the individual compounds of groups I to VI in the composition are given in relation to the total quantity of the compounds of groups I to VI. In a preferred embodiment the compounds of groups I to IV sum up to 100 wt.-%.

[0082] The composition is preferably applied to the oil or gas to be treated in amounts of 0.5 to 50 wt.-ppm, more preferably 1 to 30 wt.-ppm and especially 2 to 20 wt.-ppm as for example 0.5 to 3 wt.-ppm, 0.5 to 20 wt.-ppm, 1 to 50 wt.-ppm, 1 to 20 wt.-ppm, 2 to 50 wt.-ppm or 2 to 30 wt.-ppm per 1 ppm of sulfur contained in the oil or gas.

[0083] The use of undiluted compositions according to the invention has proven especially successful in gas contact towers.

[0084] In a preferred embodiment the compositions according to the different aspects of the

invention are used in formulations additionally comprising water. The water in the formulation may be formed during the manufacture of hemiacetals, or it can be added to the composition to balance the formulation. Preferably water is present in a concentration from 1 to 90 wt.-%, preferably between 5 and 80 wt.-% as for example between 1 and 80 wt.-% or 5 and 90 wt.-% of the formulation. In another preferred embodiment water is present to balance up to 100 wt.-% of the formulation.

[0085] Alternatively, any balance remaining in a formulated composition according to the different aspects of the invention is made up with water and/or glycol and/or alcohol based solvents in the amounts given above for water alone. Preferred alcohols and glycols are selected from, but not limited to, methanol, ethanol, propan-1-ol, propan-2-ol, ethylene glycol, diethylene glycol, triethylene glycol, neopentyl glycol, 2-butoxyethanol and their mixtures.

[0086] The compositions can be made by mixing of the compounds of groups I and II, of groups I, II and III, of groups I, II and IV respectively of groups I, II, II and IV each optionally with compounds of groups V and/or VI. The sequence of addition of the individual compounds is not important. In a preferred embodiment the compounds of groups I and II are produced simultaneously in a single pot reaction and subsequently the compounds of groups III and/or IV and optionally V and/or VI are added. For the production of formulations water and/or other solvents can be added to the composition. Alternatively, some or all of the components to make up the composition may contain solvent.

[0087] A formulated product containing the composition and solvent is preferably applied in concentrations between 5 and 40,000 mg/L, preferably between 50 and 30,000 mg/L and especially between 100 and 25,000 mg/L as for example between 5 and 40,000 mg/L, between 5 and 25,000 mg/L, between 50 and 40,000 mg/L, between 50 and 25,000 mg/L, between 100 and 40,000 mg/L and between 100 and 30,000 mg/L based on the volume of oil or gas production to be treated. The preferred and best suited concentration of the formulation depends on the formulation activity itself, the type and amount of sulfhydryl compounds to be scavenged, static conditions, temperature and salinity of the system. Furthermore, the material grade of the equipment used for operating the scavenging process should be taken into account: If e.g. a contact tower is made of stainless steel a more concentrated product can be applied while it has proven to be advantageous to apply more dilute product formulations, preferably containing a corrosion inhibitor of group VI, if a poor material of construction as for example carbon steel is used.

[0088] At the given concentration range, the use of the composition provides substantial scavenging of sulfhydryl compounds from the produced liquids and ensures a specified sulfur content of the produced hydrocarbon as it is brought to the market and therefore safe handling. Furthermore flowability of the treated hydrocarbon will not be impaired due to prevention of the formation of solid reaction products.

[0089] The present invention also includes a process for application of the composition in scavenging of sulfhydryl compounds present in the drilling and the production cycle of mineral

oil, particularly as a component of well work-over, well intervention, production enhancement and flow assurance packages.

[0090] The composition according to the invention may be injected into a sulfhydryl compound containing stream together with other ingredients known to those familiar with the art. Such other ingredients include acids, dispersants, viscosifiers, lubricity agents, scale inhibitors, friction reducers, cross linker, surfactants, pH adjuster, iron control agents, breakers; this is especially advantageous if any produced water (or recycled water) is in contact with the compositions of the instant invention.

[0091] Employing the embodiments of the instant invention allows either i) for a lower dosage rate of scavenger to obtain the same level of residual amount of sulfhydryl compound or ii) for a lower level of residual amount of sulfhydryl compound with the same dosage rate of scavenger in comparison to hemiacetals and/or acetals according to the state of the art. Additionally, in combination with a reaction product from formaldehyde and an amine the kinetics of scavenging H_2S and/or mercaptans provided by the mixture of hemiacetals and/or acetals of a monohydric alcohol and a polyhydric alcohol with an aldehyde and/or ketone can be significantly accelerated. This allows for a much more efficient scavenging of sulfhydryl compounds especially in applications where only short contact times between the oil or gas and the scavenger are available, as for example in contact towers and direct injection applications for treatment of gases. By admixture of a solids suppression agent as a further synergistic additive the gas breakthrough time of a system containing sulfhydryl compounds is extended. While improving the scavenging of sulfhydryl compounds no formation of complex and difficult to treat emulsions is observed. Furthermore the embodiments of the instant invention will not corrode the oilfield equipment that it comes into contact with, nor will it allow the deposition of unwanted solids, such as polymethylenesulfide oligomers and metal sulfide scales, so often found with applications of the prior art. Other applications of the embodiments of the instantaneous invention include treating water for downhole injection for pressure support, treatment of drilling and work-over operations, wettability alteration and well cleanout.

[0092] Within this specification, percentages are weight percentages unless specified otherwise.

EXAMPLES

Preparation of hemiacetals

[0093] In a stirred reactor alcohols were charged with the quantity given in table 1 together with 0.25 wt.-% of sodium hydroxide solution at 50 wt.-%. This mixture was homogenized for 10 minutes before paraformaldehyde (93 wt.-%) was added in the amounts given in table 1 over a period of approximately 30 minutes. The reaction mixture was warmed while stirring for

2 hours at a temperature between 80 to 85 °C. After the reaction time, the mixture was cooled to 30 °C.

[0094] In the reaction products the molar amounts of hemiacetal in respect to the total amount of hydroxyl groups charged and the content of free formaldehyde (CH₂O) were determined by

¹H NMR spectroscopy.

Table 1: Preparation of hemiacetals and acetals

(Hemi-) acetal	Reactor charge					reaction product	
	monohydric alcohol; charge [g]	polyhydric alcohol; charge [g]		paraform aldehyde [g]		(hemi-) acetal	CH ₂ O [wt.-%]
A1	methanol	500	-		500	98 %	0.07
A2	ethanol	600	-		420	99 %	0.06
A3	i-propanol	600	-		320	99 %	0.08
A4	2-EH	800	-		200	98 %	0.11
A5	-		ethyleneglycol	500	520	97 %	0.12
A6	-		diethyleneglycol	600	360	96 %	0.16
A7	-		glycerol	600	410	66 %	0.05
A8	-		pentaerythritol	500	480	98 %	0.12
A9	-		pentaerythritol	600	430	75 %	0.04
A10	ethanol	100	ethyleneglycol	490	430	75 %	0.02
A11	ethanol	80	ethyleneglycol	400	470	99 %	0.03
A12	methanol	70	glycerol	550	450	70 %	0.02
A13	methanol	80	glycerol	570	370	55 %	0.02
A14	ethanol	120	Glycerol	450	440	80 %	0.02
A15	ethanol	160	pentaerythritol	350	440	98 %	0.03
2-EH = 2-ethyl hexanol							

[0095] Further materials used were

- hexahydro-1,3,5-trimethyl-s-triazin (HTT) and 3,3'-methylenebis-5-methyloxazolidine (MBO) as the synergists according to group III.
- NaOH (5 wt.-% aqueous solution), triethylamine (TEA), monoethanolamine (MEA) and piperazine (PIP) were used as the solids suppressants according to group IV. All these materials were commercial grades.

Scavenger performance tests - efficiency

[0096] In order to demonstrate the improved efficiency of the instant invention in removing sulfhydryl compounds compared to group I respectively group II compounds alone, the removal of H₂S from an oil and from an oil/water mixture was measured.

[0097] The oil used was a mixture of kerosene with 10 % of xylene with zero bottom sediment and water (BS&W) to simulate oil field conditions.

[0098] The oil/water mixture was a mixture of the oil described above and brine (in a 50:50 volume ratio of oil to aqueous phase) to mimic the efficiency in hydrated crude oil.

[0099] In a 500 mL stirred autoclave (Parr reactor), 350 mL of the oil respectively the oil/brine mixture was de-aerated for 1 hour with N₂, then saturated with a sour gas mixture of 0,2 wt.-% H₂S and 99,8 wt.-% CO₂, by purging this gas into the oil resp. oil/brine mixture with a flow rate of 0.6 L/min. After equilibration by the sour gas mixture, 1.000 ppm of the composition to be tested was injected into the autoclave by an HPLC pump. If mixtures of (hemi-)acetals were used, their proportions by weight are given in tables 2 and 3; the amounts of synergist and solids suppressant refer to their portion in the composition and are therefore included in said dosage rate.

[0100] The performance tests were carried out at 30 °C and under 1 bar, using a gas chromatograph to measure the outlet H₂S content in the gas phase every two minutes. Then, a graph of the measured values of H₂S content (ppm) versus time (min) was plotted. The amount of hydrogen sulfide scavenged is the area above the resultant performance curve, which is calculated by the integration of the curve. For all samples the integration of the curve was done up to 60 min after the injection of H₂S-scavenger. As the output parameter of this performance test L_{SC}/kgH₂S (Liters of H₂S scavenger required to remove 1 kg of H₂S from the system) has been determined for 6 minutes and 1 hour of analysis. All consumption values are averages of three repeat tests. The test results have been summarized in Table 2 and Table 3. Percentages mean weight percent if not indicated otherwise.

Table 2: Performance tests for H₂S-scavengers in oil (zero BS&W)

Example	(Hemi)acetal	Synergist (2 wt.-%)	solids suppressant	L _{SC} /kg H ₂ S	
				@ 6 min.	@ 1 hour
P1 (comp.)	A2	-	-	20,76	9,56
P2 (comp.)	A3	-	-	21,23	10,04
P3 (comp.)	A4	-	-	32,60	16,20
P4 (comp.)	A5	-	-	18,65	9,01
P5 (comp.)	A6	-	-	18,09	8,47

Example	(Hemi)acetal	Synergist (2 wt.-%)	solids suppressant	L _{SC} /kg H ₂ S	
				@ 6 min.	@ 1 hour
P6 (comp.)	A1 + A2 (1:1)	-	-	19,12	9,85
P7 (comp.)	A5 + A6 (2:1)	-	-	17,24	8,86
P8	A2 + A5 (1:4)	-	-	14,10	7,02
P9	A2 + A5 (1:1)	-	-	14,48	7,35
P10	A4 + A5 (1:3)	-	-	13,86	7,13
P11	A10	-	-	12,95	6,89
P12	A11	-	-	13,22	6,70
P13	A3 + A6	-	-	14,27	7,54
P14(comp.)	A2	MBO	-	5,65	4,63
P15(comp.)	A3	MBO	-	5,86	4,86
P16 (comp.)	A4	MBO	-	9,98	8,05
P17 (comp.)	A5	MBO	-	5,10	4,21
P18 (comp.)	A6	MBO	-	5,28	4,36
P19	A2 + A5 (1:4)	MBO		3,10	2,72
P20	A2 + A5 (1:1)	MBO	-	3,21	2,86
P21	A4 + A5 (1:3)	MBO	-	3,25	2,80
P22	A10	MBO	-	2,98	2,61
P23	A11	MBO	-	2,92	2,55
P24	A3 + A6 (1:3)	MBO	-	3,11	2,75
P25 (comp.)	A2	MBO	5 % MEA	4,76	4,06
P26 (comp.)	A3	MBO	8 % PIP	4,80	4,12
P27 (comp.)	A4	MBO	10 % TEA	8,12	6,95

Example	(Hemi)acetal	Synergist (2 wt.-%)	solids suppressant	L _{SC} /kg H ₂ S	
				@ 6 min.	@ 1 hour
P28 (comp.)	A5	MBO	5 % MEA	4,29	3,68
P29 (comp.)	A6	MBO	8 % PIP	4,23	3,57
P30	A2 + A5 (1:4)	MBO	5 % MEA	2,27	1,97
P31	A2 + A5 (1:1)	MBO	5 % MEA	2,35	2,04
P32	A4 + A5 (1:3)	MBO	10 % TEA	2,64	2,25
P33	A10	MBO	5 % MEA	2,12	1,89
P34	A11	MBO	5 % MEA	2,26	2,00
P35	A3 + A6 (1:3)	MBO	8 % PIP	2,49	2,21

Table 3: Performance tests for H₂S-scavenging in a mixture of the oil and brine (50:50 volume ratio of oil to aqueous phase)

Example	(Hemi)acetal	Synergist	solids suppressant	L _{SC} /kg H ₂ S	
				@ 6 min.	@ 1 hour
P36 (comp.)	A1	-	-	23,36	10,04
P37 (comp.)	A2	-	-	23,82	10,20
P38 (comp.)	A5	-	-	23,11	9,50
P39 (comp.)	A7	-	-	20,80	8,91
P40 (comp.)	A8	-	-	19,64	8,52
P41 (comp.)	A9	-	-	19,22	8,20
P42	A2 + A5 (1:4)	-	-	15,22	6,69
P43	A10	-	-	15,47	6,77
P44	A1 + A7(1:3)	-	-	14,96	6,61
P45	A1 + A7 (1:1)	-	-	15,82	6,96
P46	A12	-	-	14,92	6,48
P47	A13	-	-	15,44	6,88
P48	A2 + A8 (1:1)	-	-	15,71	6,90
P49	A2 + A8 (1:5)	-	-	14,88	6,56

Example	(Hemi)acetal	Synergist	solids suppressant	L _{SC} /kg H ₂ S	
				@ 6 min.	@ 1 hour
P50	A2 + A9 (1:1)	-	-	16,05	7,01
P51	A14	-	-	14,66	6,50
P52 (comp.)	A1	HTT	-	8,76	7,04
P53 (comp.)	A2	MBO	-	8,40	6,88
P54 (comp.)	A5	MBO	-	8,56	6,80
P55 (comp.)	A7	HTT	-	9,30	7,56
P56 (comp.)	A8	HTT	-	8,07	6,52
P57 (comp.)	A9	HTT	-	8,41	6,92
P58	A2 + A5 (1:4)	MBO	-	6,28	5,44
P59	A10	MBO	-	6,15	5,26
P60	A1 + A7 (1:3)	HTT	-	6,25	5,30
P61	A1 + A7 (1:1)	HTT	-	6,38	5,45
P62	A12	HTT	-	5,84	5,12
P63	A13	HTT	-	6,50	5,78
P64	A2 + A8 (1:1)	HTT	-	5,95	5,17
P65	A2 + A8 (1:5)	HTT	-	5,85	5,03
P66	A2 + A9 (1:1)	HTT	-	5,92	5,28
P67	A14	HTT	-	6,14	5,19
P68 (comp.)	A1	HTT	5 % NaOH	6,91	5,72
P69 (comp.)	A2	MBO	10 % MEA	6,52	5,56
P70 (comp.)	A5	MBO	10 % MEA	7,05	5,92
P71 (comp.)	A7	HTT	5 % NaOH	7,33	6,24
P72 (comp.)	A8	HTT	10 % MEA	6,31	5,25
P73 (comp.)	A9	HTT	10 % MEA	6,73	5,57
P74	A2 + A5 (1:4)	MBO	10 % MEA	4,42	3,86
P75	A10	MBO	10 % MEA	3,96	3,54
P76	A1 + A7 (1:3)	HTT	5 % NaOH	4,26	3,68

Example	(Hemi)acetal	Synergist	solids suppressant	L _{sc} /kg H ₂ S	
				@ 6 min.	@ 1 hour
P77	A1 + A7 (1:1)	HTT	5 % NaOH	4,49	3,89
P78	A12	HTT	5 % NaOH	3,93	3,47
P79	A13	HTT	5 % NaOH	4,07	3,62
P80	A2 + A8 (1:1)	HTT	10 % MEA	4,18	3,65
P81	A2 + A8 (1:5)	HTT	10 % MEA	3,72	3,35
P82	A2 + A9 (1:1)	HTT	10 % MEA	4,10	3,67
P83	A15	HTT	10 % MEA	3,86	3,38
P84	A2 + A5 (1:4)	-	10 % MEA	7,86	4,42
P85	A10	-	10 % MEA	7,73	4,28
P86	A14	HTT	-	6,23	5,35
P87	A14	-	10 % TEA	7,82	4,38

[0101] In the tests including a synergist the portion of MBO was 2 wt.-%, the portion of HTT was 6 wt.-% of the scavenger formulation

[0102] In tables 2 and 3 the lower consumption of the scavenger to remove 1 kg of H₂S, the more efficient is the scavenger. In the inventive examples the mixtures of acetals being based on mixtures of monohydric alcohols and polyhydric alcohols are more efficient than the single components. The efficiency is further improved by the incorporation of a synergist and/or a solids suppressant. Furthermore, incorporation of the synergist enhances the reaction rate in the initial phase of the test as can be seen from the difference between scavenging efficiency after 6 minutes versus 1 hour.

Scavenger performance tests - Gas Breakthrough

[0103] The performance of the H₂S scavengers according to the invention is evaluated for their ability to remove H₂S from a flowing gas stream by passing gas laden with H₂S through a column of fluid containing the scavenger chemical. A sour gas mixture of 0,2 % H₂S and 99,8 % CO₂ is purged with a flow rate of 60 mL/min through 440 mL of a 22 % active solution of the scavenger composition in water. Under these conditions the average contact time of gas and scavenger is about 4 seconds. Initially all of the H₂S is removed from the gas stream and no

H₂S is detected in the effluent gas. At some point in time (the breakthrough time or TBT) the chemical can no longer entirely remove H₂S from the gas stream and H₂S is observed in the effluent. This parameter is a measure of the efficacy of the scavenger especially for contact tower applications with short contact time. The longer the break through time the more efficient is the chemical scavenger.

[0104] The effect of the solids suppression agent is rated by visual inspection of the spent scavenger fluid after the gas breakthrough test. The degree of solids formation is rated opaque > turbid > opalescent > clear.

[0105] The overall concentration of the scavenger formulations in all examples is 22 wt.-%, i. e. in examples where synergist and/or solids suppressant is present the concentration of (hemi-)acetals is reduced accordingly.

Table 4: Gas breakthrough times for different (hemi-)acetals

example	(hemi-)acetal	synergist	solids suppressant	TBT [min]	visual inspection
B1 (comp.)	A1	-	-	31	opaque
B2 (comp.)	A2	-	-	29	opaque
B3 (comp.)	A3	-	-	27	opaque
B4 (comp.)	A5	-	-	17	opaque
B5 (comp.)	A7	-	-	35	opaque
B6 (comp.)	A1 + A2 (1:1)	-	-	31	opaque
B7 (comp.)	A5 + A7 (1:1)	-	-	37	opaque
B8	A2 + A5 (1:1)	-	-	45	opaque
B9	A2 + A5 (1:4)	-	-	47	opaque
B10	A10	-	-	52	opaque
B11	A11	-	-	58	opaque
B12	A12	-	-	55	opaque
B13	A1 + A7 (1:4)	-	-	58	opaque
B14	A3 + A7 (1:2)	-	-	49	opaque
B15	A1	7 % MBO	-	76	turbid
B16	A2	3 % HTT	-	69	turbid
B17	A3	5 % HTT	-	74	turbid
B18	A5	3 % HTT	-	78	turbid
B19	A7	7 % MBO	-	77	turbid
B20	A2 + A5 (1:1)	3 % HTT	-	82	turbid
B21	A2 + A5 (1:4)	3 % HTT	-	89	turbid

example	(hemi-)acetal	synergist	solids suppressant	TBT [min]	visual inspection
B22	A10	3 % HTT	-	87	turbid
B23	A11	3 % HTT	-	84	turbid
B24	A12	7 % MBO	-	81	turbid
B25	A1 + A7 (1:4)	5 % MBO		85	turbid
B26	A3 + A7 (1:2)	5 % HTT	-	80	turbid
B27	A1	-	10 % MEA	149	opalescent
B28	A2	-	15 % PIP	146	opalescent
B29	A3	-	15 % PIP	134	opalescent
B30	A5	-	15 % PIP	157	opalescent
B31	A7	-	10 % MEA	150	opalescent
B32	A2 + A5 (1:1)	-	15 % PIP	164	opalescent
B33	A2 + A5 (1:4)	-	15 % PIP	182	opalescent
B34	A10	-	15 % PIP	169	opalescent
B35	A11	-	15 % PIP	178	opalescent
B36	A12	-	10 % MEA	171	opalescent
B37	A1 + A7 (1:4)	-	15 % PIP	172	opalescent
B38	A3 + A7 (1:2)	-	15 % PIP	163	opalescent
B39	A1	7 % MBO	10 % MEA	215	clear
B40	A2	3 % HTT	15 % PIP	200	clear
B41	A3	5 % HTT	15 % PIP	192	clear
B42	A5	3 % HTT	15 % PIP	226	clear
B43	A7	7 % MBO	10 % MEA	222	clear
B44	A2 + A5 (1:1)	3 % HTT	15 % PIP	298	clear
B45	A2 + A5 (1:4)	3 % HTT	15 % PIP	321	clear
B46	A10	3 % HTT	15 % PIP	334	clear
B47	A11	3 % HTT	15 % PIP	348	clear
B48	A12	7 % MBO	10 % MEA	342	clear
B49	A1 + A7 (1:4)	5 % MBO	15 % PIP	346	clear
B50	A3 + A7 (1:2)	5 % HTT	15 % PIP	316	clear

[0106] A comparison of the inventive examples and the comparative examples shows that mixtures of (hemi-)acetals containing reaction products of monohydric and polyhydric alcohols have a higher TBT than the single components or mixtures of components of the same group. The addition of a synergist according to group III increases the H₂S scavenging activity of (hemi-)acetals and especially of mixtures of (hemi-)acetals significantly. The scavenging process becomes faster and more efficient. The addition of a solids suppressant further significantly improves the performance of the scavenger. Formation of solids is mostly inhibited which otherwise hampers the accessibility of part of the scavenger and furthermore bears the risk of clogging flow lines for the effluent. The enhancement in scavenging efficiency exceeds the stoichiometric H₂S scavenging capacity of the added synergist considerably.

REFERENCES CITED IN THE DESCRIPTION

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P a t e n t k r a v

1. Anvendelse af en sammensætning til opfangning hydrogensulfid og/eller mercaptaner, hvilken sammensætning omfatter

5 I. mindst et reaktionsprodukt mellem en nitrogenfri monovalent alkohol og en aldehyd eller keton og

II. mindst et reaktionsprodukt mellem en nitrogenfri polyvalent alkohol og en aldehyd eller keton, hvor

10 reaktionsprodukterne I. og II. er udvalgt blandt hemiacetaler og acetal, og aldehyden eller ketonen indeholder 1 til 10 carbonatomer, og den monovalente alkohol omfatter 1 til 15 carbonatomer, og den polyvalente alkohol indeholder 2 til 20 carbonatomer og 2 til 6 hydroxygrupper.

15 **2.** Anvendelse ifølge krav 1, yderligere omfattende

III. mindst et reaktionsprodukt fra formaldehyd og en forbindelse udvalgt fra gruppen bestående af ammoniak og en amin, hvor aminen er udvalgt fra gruppen bestående af primære alkylaminer med 1 til 4 carbonatomer og primære hydroxyalkylaminer med 2 til 4 carbonatomer.

20

3. Anvendelse ifølge krav 1 eller 2, yderligere omfattende

IV. mindst en uorganisk eller organisk alkalisk forbindelse, der fungerer som et tørstofhæmningmiddel.

25 **4.** Anvendelse ifølge et eller flere af kravene 1 - 3, hvor aldehyden eller ketonen indeholder 1 til 4 carbonatomer.

5. Anvendelse ifølge et eller flere af kravene 1 - 4, hvor aldehyden eller ketonen er udvalgt fra gruppen bestående af formaldehyd, paraformaldehyd, glyoxal, acetaldehyd, propionaldehyd, butyraldehyd og glutaraldehyd.

30

6. Anvendelse ifølge et eller flere af kravene 1 - 5, hvor aldehyden eller ketonen er formaldehyd.

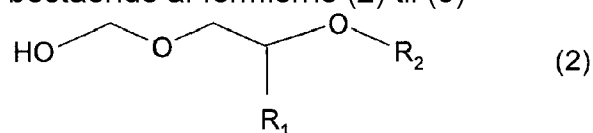
7. Anvendelse ifølge et eller flere af kravene 1 - 6, hvor den monovalente alkohol omfatter 1 til 5 carbonatomer.

5 8. Anvendelse ifølge et eller flere af kravene 1 - 7, hvor den monovalente alkohol er en alifatisk alkohol.

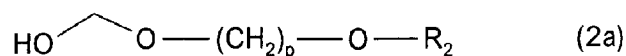
10 9. Anvendelse ifølge et eller flere af kravene 1 - 8, hvor den monovalente alkohol er udvalgt fra gruppen bestående af methanol, ethanol, propanol, isopropanol, n-butanol, iso-butanol, tert-butanol, pentanol, hexanol, heptanol og octanol og en hvilken som helst blanding deraf.

15 10. Anvendelse ifølge et eller flere af kravene 1 - 9, hvor den polyvalente alkohol er udvalgt fra gruppen bestående af monoethylenglycol, diethylenglycol, triethylenglycol, propylenglycol, butylenglycol, neopentyl glycol, pentaerythritol, glycerol og oligomerer af glycerol.

11. Anvendelse ifølge et eller flere af kravene 1 - 3, hvor reaktionsproduktet mellem en polyvalent alkohol og en aldehyd eller keton er udvalgt fra gruppen bestående af formlerne (2) til (5)



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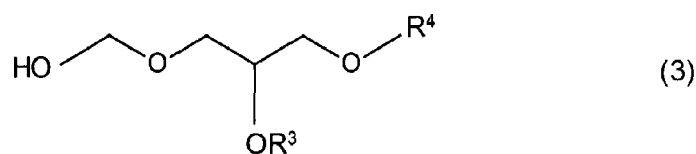
hvor

p er et tal fra 2 til 10, og

R₁ er H eller C₁- til C₈-alkyl, og

R₂ er CH₂OH, og

25

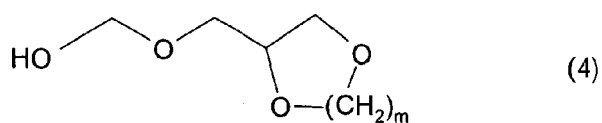


hvor

R₃ og R⁴ uafhængigt er H eller CH₂OH

30

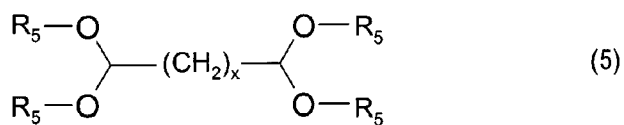
3



hvor

m er 1 til 10, fortrinsvis 1 eller 2, og

5



hvor

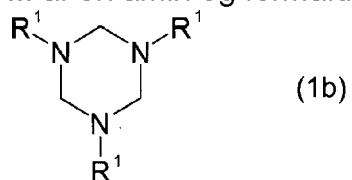
R₅ er H, CH₃, (CH₂)_zCH₃

z er 1 til 10

10

x er 1 til 5.

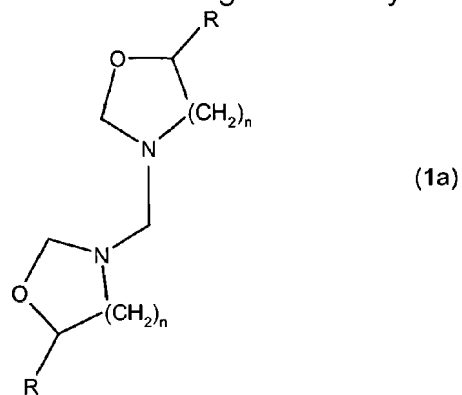
12. Anvendelse ifølge et eller flere af kravene 2 - 11, hvor reaktionsproduktet III af en amin og formaldehyd svarer til formel (1b)



15

hvor hvert R¹ er C₁- til C₄-alkyl eller C₂- til C₄-hydroxyalkyl.

13. Anvendelse ifølge et eller flere af kravene 2 - 11, hvor reaktionsproduktet III af en amin og formaldehyd svarer til formel (1a)



20

hvor

R er H eller methyl, og

n er 1 eller 2.

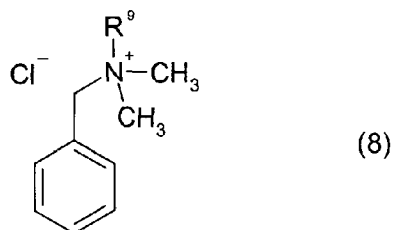
14. Anvendelse ifølge krav 13, hvor forbindelsen med formel 1 er 3,3'-methylenbis-5-methyl-oxazolidin.

5

15. Anvendelse ifølge et eller flere af kravene 2 - 14, hvor reaktionsproduktet III af en amin og formaldehyd er til stede i sammensætningen i en mængde fra 1 vægt-% til 20 vægt-%, fortrinsvis mellem 5 vægt-% og 15 vægt-%.

10

16. Anvendelse ifølge et eller flere af kravene 1 - 15, yderligere omfattende en alkyldimethylbenzylammoniumchlorid i henhold til formel (8) som en korrosionsinhibitor



hvor R⁹ er C₈- til C₁₈-alkyl.

15

17. Anvendelse ifølge krav 16, hvor forbindelsen med formel (8) er til stede i en mængde mellem 0,01 og 5 vægt-%, fortrinsvis mellem 0,5 og 2 vægt-%.

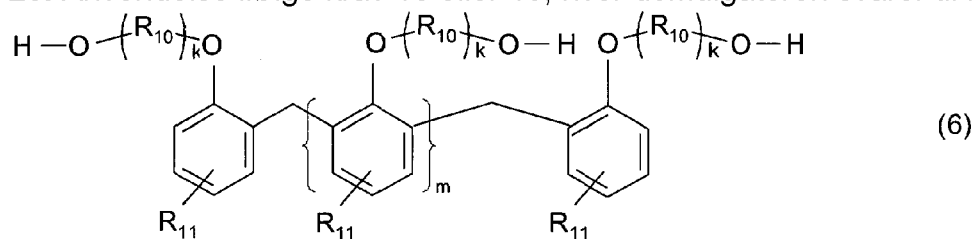
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18. Anvendelse ifølge et eller flere af kravene 1 - 17, yderligere omfattende en demulgator i en mængde mellem 0,1 til 10 vægt-%, fortrinsvis mellem 0,5 og 2 vægt-%.

25

19. Anvendelse ifølge krav 18, hvor demulgatoren er udvalgt fra gruppen bestående af polysorbater, fedtalkoholer, polymerer omfattende ethylenoxid, polymerer omfattende propylenoxid, ethylenoxid-propylenoxid-copolymerer, alkylpolyglucosider, alkylphenoethoxylater, alkylpolyethylenoxid, alkylbenzen-sulfonsyre og ethoxylet og/eller propoxylet alkylphenolformaldehyd-resiner.

20. Anvendelse ifølge krav 18 eller 19, hvor demulgatoren svarer til formel (6)



hvor

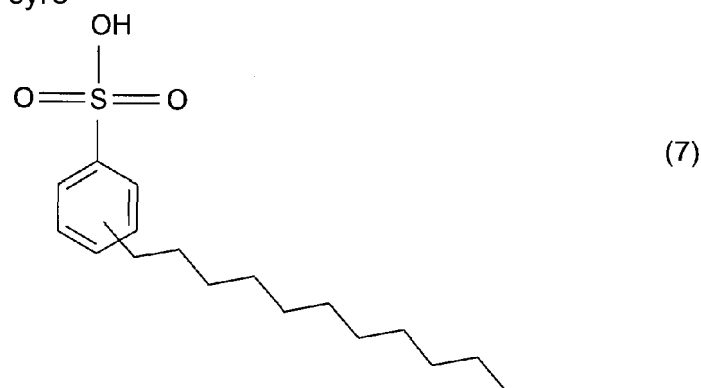
R_{10} er C_2 - til C_4 -alkylen,

R_{11} er C_1 - til C_{18} -alkyl,

k er et tal fra 1 til 200,

m er et tal fra 1 til 100.

21. Anvendelse ifølge krav 18, hvor demulgatoren er dodecylbenzensulfon-syre



22. Anvendelse ifølge et eller flere af kravene 18 - 21, hvor demulgatoren er en blanding af mindst en forbindelse med formel (6) og mindst en forbindelse med formel (7) i et vægtforhold på fra 5:1 til 1:5, fortrinsvis i et vægtforhold på fra 3:1 til 1:3.

23. Anvendelse ifølge et eller flere af kravene 3 - 22, hvor den alkaliske forbindelse IV. er udvalgt fra gruppen bestående af

IV(a). alkaliske metalsalte eller alkaliske jordmetalsalte

IV(b). ammoniak; alkyl-, aryl- eller alkylarylaminer

IV(c). hydroxyalkyl-, hydroxylaryl- eller hydroxyalkylarylaminer

IV(d). multifunktionelle aminer, der ud over en aminogruppe, indeholder mindst en yderligere funktionel gruppe udvalgt fra gruppen bestående af aminogrupper, ethergrupper og syregrupper eller en ester, amid eller salt deraf

IV(e). blandinger af forbindelser af grupperne IV(a) til IV(c).

5 hvor "alkyl" betyder C₁- til C₂₀-alkyl, "aryl" betyder C₆- til C₂₀-aryl og "alkylaryl" betyder C₇- til C₂₀-alkylaryl.

10 **24.** Anvendelse ifølge et eller flere af kravene 1 - 23, omfattende 1 til 50 vægt-% af reaktionsproduktet mellem en monovalent alkohol eller en aldehyd eller keton, fortrinsvis mellem 5 og 25 vægt-%.

15 **25.** Anvendelse ifølge et eller flere af kravene 1 - 24, omfattende 1 til 95 vægt-% af reaktionsproduktet mellem en polyvalent alkohol og en aldehyd eller keton, fortrinsvis mellem 20 og 75 vægt-%.

26. Anvendelse ifølge et eller flere af kravene 1 - 25, omfattende 0,1 til 10 vægt-%, fortrinsvis 0,5 til 5 vægt-% af mindst et tørstofhæmningmiddel.

20 **27.** Anvendelse ifølge et eller flere af kravene 1 - 26, omfattende vand op til 100 vægt-%.

28. Anvendelse af en sammensætning ifølge et eller flere af kravene 1 - 27, hvor opfangningen sker fra fluider eller gasser genereret fra underjordiske formationer.

25 **29.** Anvendelse ifølge et eller flere af kravene 1 - 28, hvor opfangningen fra gas foretages i et kontakttårn eller ved direkte indsprøjtning ind i gassen.

30 **30.** Fremgangsmåde til opfangning af hydrogensulfid og/eller mercaptaner, omfattende tilsætning til et medium omfattende sådan hydrogensulfid eller mercaptaner af en sammensætning omfattende

I. mindst et reaktionsprodukt mellem en nitrogenfri monovalent alkohol og en aldehyd eller keton og

35 II. mindst et reaktionsprodukt mellem en nitrogenfri polyvalent alkohol og en aldehyd eller keton, hvor

reaktionsprodukterne I. og II. er udvalgt blandt hemiacetaler og acetal, og aldehyden eller ketonen indeholder 1 til 10 carbonatomer, og den monovalente alkohol omfatter 1 til 15 carbonatomer, og den polyvalente alkohol indeholder 2 til 20 carbonatomer og 2 til 6 hydroxygrupper.

5

31. Anvendelse af et reaktionsprodukt fra formaldehyd og en forbindelse udvalgt fra gruppen bestående af ammoniak og en amin, hvor aminen er udvalgt fra gruppen bestående af primære alkylaminer med 1 til 4 carbonatomer og primære hydroxyalkylaminer med 2 til 4 carbonatomer, som en synergist i reaktionen mellem hydrogensulfid og/eller et mercaptan og en sammensætning omfattende

10

I. mindst et reaktionsprodukt mellem en nitrogenfri monovalent alkohol og en aldehyd eller keton og

15

II. mindst et reaktionsprodukt mellem en nitrogenfri polyvalent alkohol og en aldehyd eller keton,

hvor reaktionsprodukterne I. og II. er hemiacetaler og/eller acetal, og aldehyden eller ketonen indeholder 1 til 10 carbonatomer, og

den monovalente alkohol omfatter 1 til 15 carbonatomer, og

20

den polyvalente alkohol indeholder 2 til 20 carbonatomer og 2 til 6 hydroxygrupper.