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(54) HYDROGEN SULPHIDE AND MERCAPTAN SCAVENGING ADDITIVE CONCENTRATE COMPRISING AN OXAZOLIDINE COMPOUND AND AN (ETHOXYLATED) PHENOL COMPOUND

(57) The present invention relates to an additive concentrate useful for scavenging hydrogen sulphide and organic compounds comprising at least one sulfhydryl group, comprising an oxazolidine compound a particular additive chosen from (ethoxylated) phenol compounds.

The invention also relates to a composition comprising said concentrate additive and a liquid solvent, as well as the use of the additive concentrate or of the composition of the invention for scavenging hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group in a liquid or gaseous stream.

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Description

[0001] The present invention relates to an additive concentrate useful for scavenging hydrogen sulphide and organic compounds comprising at least one sulfhydryl group. Said additive concentrate comprises an oxazolidine compound and a particular additive chosen from (ethoxylated) phenol compounds.

[0002] The invention also relates to a composition comprising said additive concentrate and a liquid solvent.

[0003] The present invention also relates to the use of the additive concentrate or of the composition of the invention for scavenging hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group in a liquid or gaseous stream.

[0004] The invention also relates to the use of the (ethoxylated) phenol compound additive for improving the efficiency of oxazolidine compounds in scavenging hydrogen sulphide and organic compounds comprising at least one sulfhydryl group in a liquid or gaseous stream.

[0005] The present invention also relates to a method for scavenging hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group comprising contacting a hydrocarbon stream such as crude oil, fuel or natural gas with the additive concentrate or with the composition of the invention.

[0006] Hydrogen sulphide (H_2S) is a colourless and fairly toxic, flammable and corrosive gas which has a characteristic odour at a very low concentration. Hydrogen sulphide dissolves in liquid and gaseous streams such as hydrocarbon and water streams and can also be present in the vapour phase above liquid streams as well as in hydrocarbon gas such as LPG and natural gas. The hydrogen sulphide emissions can be harmful to workers operating in the drilling, production, transport, storage, and processing of such streams. It would therefore be desirable for the workers' comfort and safety to reduce or even eliminate the hydrogen sulphide emissions during the handling of said products.

[0007] Legislation has been in place for years, imposing strict regulations on hydrogen sulphide levels of hydrocarbon streams in pipelines, in storage and shipping containers.

[0008] Similar problems arise with organic compounds comprising a sulfhydryl group (-SH) such as mercaptans R-SH, thiocarboxylic acids RC(O)SH, dithiocarboxylic acids RC(S)SH, with R denoting a hydrocarbon chain. Such sulfhydryl-containing compounds are very corrosive, and are likely to release hydrogen sulphide.

[0009] A variety of chemical scavengers are available to reduce the concentration of hydrogen sulphide and sulfhydryl-containing compounds in liquid and gaseous streams containing them, in particular aqueous streams and hydrocarbon streams such as gas, crude oils and refined products. Some of the most common methods for treating hydrogen sulphide consist in contacting them with a chemical scavenger such as compounds containing a triazine group, glyoxal, as well as metal-based scavengers. Glyoxal has been used extensively as hydrogen sulphide scavenger but suffers from a major drawback since aqueous glyoxal solutions are highly corrosive and cannot be used for a gas tower application. Triazines have recently become more common chemical scavengers used for treating hydrogen sulphide from hydrocarbon streams.

[0010] Other hydrogen sulphide scavengers have been developed, and among them scavengers based on oxazolidine, like 3,3'-methylenebis(5-methyloxazolidine), known as MBO. A method for scavenging hydrogen sulphide from sour hydrocarbon substrates has been described in WO 98/02501.

[0011] However, this technology requires an important contact time in order to be efficient in sulphur removal and thus involves injection of higher doses.

[0012] Formulations of MBO with promoters, also named boosters, have been developed to enhance the efficiency of MBO. For example, WO 2017/102693 describes a composition comprising MBO and one or more additive selected among urea, urea derivatives, amino acids, guanidine, guanidine derivatives or 1,2-diols.

[0013] Other promoters, such as polyethylene glycol-based promoters, have been described. While enhancing the H_2S scavenging performance of MBO, these compounds have a major drawback as they present a high viscosity and are solid at room temperature. Therefore, the compositions containing MBO combined with such promoters can hardly be used at cold temperatures nor be injected using high pressure systems due to their viscosity.

[0014] There remains a continuous need for novel solutions for eliminating hydrogen sulphide and other compounds comprising a sulfhydryl group in an efficient, economic and safe manner.

[0015] The Applicant has now discovered that the combination of oxazolidine compounds with a particular additive chosen from (ethoxylated) phenol compounds was particularly efficient for scavenging hydrogen sulphide and unwanted organic compounds comprising at least one sulfhydryl group.

[0016] Therefore, the present invention relates to an additive concentrate useful for scavenging hydrogen sulphide and mercaptans in hydrocarbon streams, said composition comprising at least one oxazolidine compound and at least one (ethoxylated) phenol compound chosen from compounds having the following formula (III):

$$R\text{-}Ph\text{-}(OCH_2CH_2)_n\text{-}OH \qquad (III)$$

wherein

Ph denotes a benzene ring,
R represents a linear or branched saturated or unsaturated hydrocarbon chain comprising from 8 to 24 carbon atoms, which may be substituted or not substituted, and
n represents a number ranging from 0 to 10,
and from derivatives of such compounds of formula (III).

[0017] The additive concentrate of the present invention allows achieving an improved scavenging of hydrogen sulphide and organic compounds comprising at least one sulfhydryl group in a short contact time. The improvement can be seen when the remaining amount of sulphur compounds in the stream is reduced and/or when the speed of the scavenging of sulphur compounds is increased when contacting the composition according to the invention with said stream.

[0018] The additive concentrate of the present invention allows a faster scavenging, i.e. the amount of sulphur compounds is decreased more rapidly than with prior art scavenging compositions.

[0019] The invention also relates to a composition comprising said additive concentrate and a liquid solvent.

[0020] The present invention also relates to the use of the additive concentrate or of the composition of the invention for scavenging hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group in a liquid or gaseous stream.

[0021] The invention also relates to the use of the (ethoxylated) phenol compound additive for improving the efficiency of oxazolidine compounds in scavenging hydrogen sulphide and organic compounds comprising at least one sulfhydryl group in a liquid or gaseous stream.

[0022] The present invention also relates to a method for scavenging hydrogen sulphide and/or mercaptans comprising contacting a hydrocarbon stream such as crude oil, fuel or natural gas with the scavenging additive concentrate or the scavenging composition of the invention.

[0023] In the following, and at least one other indication, the limits of a value range are included within this range, particularly in the expressions "between" and "ranging from ... to ...".

[0024] Moreover, the expressions "at least one" and "at least" used in the present description are respectively equivalent to the expressions "one or more" and "more than or equal to".

[0025] Finally, in a manner known per se, C_N compound or group designates a compound or a group containing in its chemical structure N carbon atoms.

[0026] Within the meaning of the present invention:

- the term "acyclic alkyl" refers to an alkyl group which does not form part of a cycle,
- the term "acyclic alkenyl" refers to an alkenyl group which does not form part of a cycle,
- the term "cyclic alkyl" refers to a saturated cycloalkyl group, wherein the cycle can be optionally substituted by one or more linear or branched alkyl or alkenyl groups. Preferably, the cycle comprises 5 or 6 carbon atoms and the substituent(s) if any comprise(s) from 1 to 6 carbon atoms, preferably from 1 to 3 carbon atoms,
- the term "cyclic alkenyl" refers to an unsaturated cycloalkyl group, wherein the cycle comprising at least one unsaturation can be optionally substituted by one or more linear or branched alkyl or alkenyl groups. Preferably, the cycle comprises 5 or 6 carbon atoms and the substituent(s) if any comprise(s) from 1 to 6 carbon atoms, preferably from 1 to 3 carbon atoms.

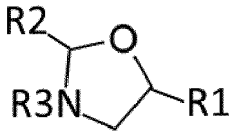
Oxazolidine compounds

[0027] The additive concentrate of the invention comprises at least one oxazolidine compound.

[0028] Within the meaning of the present invention, the expression "oxazolidine compound" refers to a compound comprising at least one oxazolidine cycle, said cycle being substituted or not substituted.

[0029] Preferably, the oxazolidine compound(s) is (are) selected from compounds comprising one oxazolidine cycle (i.e. mono-oxazolidines) or two oxazolidine cycles (i.e. bisoxazolidines).

[0030] Oxazolidine compounds useful in the present invention and comprising one oxazolidine cycle preferably correspond to the following formula (I):



(I)

wherein R1 and R2, identical or different, are selected from a hydrogen atom and linear or branched, cyclic or acyclic,

alkyl or alkenyl groups having from 1 to 6 carbon atoms, preferably from a hydrogen atom, a methyl and an ethyl group, and

R3 is selected from a hydrogen atom and linear or branched, cyclic or acyclic, saturated or unsaturated, aromatic or non aromatic hydrocarbon groups having from 1 to 30 carbon atoms, preferably from a hydrogen atom and from linear or branched, cyclic or acyclic, saturated or unsaturated, aromatic or non aromatic hydrocarbon groups having from 1 to 20 carbon atoms.

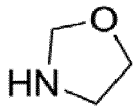
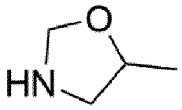
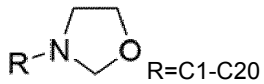
[0031] Preferably, R1 and R2, identical or different, are selected from a hydrogen atom and a methyl group.

[0032] According to a first preferred embodiment, R1 and R2 are identical and represent a hydrogen atom and R3 represents a hydrogen atom.

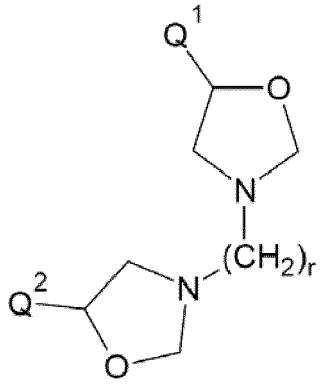
[0033] According to a second preferred embodiment, R1 represents a methyl group, R2 represents a hydrogen atom, and R3 represents a hydrogen atom.

[0034] According to a third preferred embodiment, R1 and R2 are identical and represent a hydrogen atom, and R3 is selected from linear or branched, cyclic or acyclic, saturated or unsaturated, aromatic or non aromatic hydrocarbon groups having from 1 to 20 carbon atoms.

[0035] Preferred mono-oxazolidine compounds are 1,3-oxazolidine, 5-methyloxazolidine, and 3-(C1-C20)alkyl-oxazolidines, which correspond to the following formulae:

1,3-Oxazolidine	
5-Methyloxazolidine	
3 -(C1-C20) Alkyl-Oxazolidines	 R=C1-C20

[0036] Oxazolidine compounds useful in the present invention and comprising two oxazolidine cycles preferably correspond to the following formula (II):



(II)

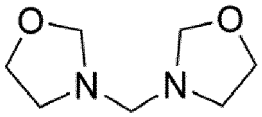
wherein:

- r is an integer ranging from 1 to 6, preferably from 1 to 2;
- Q^1 and Q^2, identical or different, are selected from a hydrogen atom and linear or branched, cyclic or acyclic, alkyl or alkenyl groups having from 1 to 6 carbon atoms, preferably from 1 to 2 carbon atoms.

[0037] Preferably, r denotes 1.

[0038] Preferred bisoxazolidine compounds are 3,3'-methylenebis(oxazolidine) and 3,3'-methylenebis(5-methyloxa-

zolidine) (also known as MBO), which correspond to the following formulae:

3,3'-Methylenebis(oxazolidine)	
3,3'-Methylenebis(5-methyloxazolidine) (MBO)	

[0039] Preferably, the oxazolidine compound(s) is (are) selected from 1,3-oxazolidine, 5-methyloxazolidine, 3-(C1-C20)alkyl-oxazolidines, 3,3'-methylenebis(oxazolidine), 3,3'-methylenebis(5-methyloxazolidine) (MBO) and mixtures thereof.

[0040] Preferably, the oxazolidine compound(s) is (are) present in an amount ranging from 95 to 99.99%wt, preferably from 98 to 99.95%wt, more preferably from 99 to 99.90%wt, relative to the total weight of the additive concentrate.

[0041] In a particular embodiment, the oxazolidine compound(s) chosen from mono-oxazolidines, bisoxazolidines and mixtures thereof are present in an amount ranging from 95 to 99.99%wt, preferably from 98 to 99.95%wt, more preferably from 99 to 99.90%wt, relative to the total weight of the additive concentrate.

[0042] In another particular embodiment, the oxazolidine compound(s) chosen from from 1,3-oxazolidine, 5-methyl-oxazolidine, 3-(C1-C20)alkyl-oxazolidines, 3,3'-methylenebis(oxazolidine), 3,3'-methylenebis(5-methyloxazolidine) (MBO) and mixtures thereof are present in an amount ranging from 95 to 99.99%wt, preferably from 98 to 99.95%wt, more preferably from 99 to 99.90%wt, relative to the total weight of the additive concentrate.

(Ethoxylated) phenol compounds

[0043] The additive concentrate of the invention comprises at least one (ethoxylated) phenol compound chosen from compounds having the following formula (III):

$$R\text{-}Ph\text{-}(OCH_2CH_2)_n\text{-}OH \qquad (III)$$

wherein

Ph denotes a benzene ring,
R represents a linear or branched saturated or unsaturated hydrocarbon chain comprising from 8 to 24 carbon atoms, which may be substituted or not substituted, and
n represents a number ranging from 0 to 20,
and from derivatives of such compounds of formula (III).

[0044] The substituents which may be present on said R hydrocarbon chain may be chosen in particular from hydroxy groups (-OH), hydroxyalkyl groups of formula -OR' wherein R' denotes a C_1 to C_4 alkyl radical, amino groups of formula $-NR_1R_2$ wherein R_1 and R_2 independently one from another denote a hydrogen atom or a C_1 to C_4 alkyl radical.

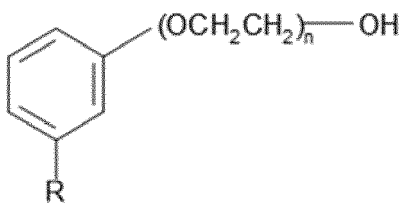
[0045] According to a preferred embodiment, R represents a linear or branched saturated or unsaturated hydrocarbon group comprising from 8 to 24 carbon atoms, preferably from 10 to 22 carbon atoms, even more preferably from 12 to 14 carbon atoms.

[0046] According to a preferred embodiment, R represents a linear saturated or unsaturated hydrocarbon group.

[0047] By unsaturated, it is referred to hydrocarbon groups including one or more olefinic bond(s) -C=C-, such as two or three olefinic bonds.

[0048] The benzene ring Ph meets the formula C_6H_4. The groups -R and - $(OCH_2CH_2)_n$-OH may be positioned on the benzene ring in ortho, meta or para position relative to each other. The meta position is preferred.

[0049] Thus, according to a preferred embodiment, the compounds of formula (III) are chosen from those having developed formula (IIIa) below:

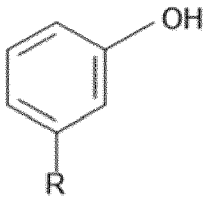


(IIIa)

wherein R and n are as defined above, including preferred embodiments detailed hereabove.

[0050] According to a first preferred embodiment, in formula (IIIa) above n denotes 0.

[0051] In this first embodiment, the(ethoxylated) phenol compound(s) are chosen from those having developed formula (IIIb) below:



(IIIb)

wherein R is as defined above, including preferred embodiments detailed hereabove.

[0052] A particularly preferred compound of formula (IIIb) is cardanol.

[0053] According a second preferred embodiment, in formula (IIIa) above n ranges from 1 to 18, preferably from 1 to 15 and most preferably from 1 to 12.

[0054] Particularly preferred compounds are (poly) ethoxylated cardanols chosen from cardanols ethoxylated with n EO wherein n is as defined above, hereafter denoted "cardanols n EO". In a usual manner, "cardanol n EO" denotes a compound consisting of cardanol ethoxylated with an average number of n moles of oxyethylene per mole of cardanol. Particularly preferred compounds are cardanol 1 EO, cardanol 2.5 EO, cardanol 5 EO, cardanol 7 EO, cardanol 12 EO, and mixtures thereof.

[0055] By derivatives of compounds of formula (III), it is meant compounds comprising in their structure one or more unit(s) of formula (III). Preferred derivatives include copolymers of compounds of formula (III).

[0056] According to a third preferred embodiment, the (ethoxylated) phenol compound(s) are chosen from resins obtainable by condensation of at least one compound of formula (III) with at least one aldehyde having from 1 to 8 carbon atoms.

[0057] The aldehyde used for obtaining said cardanol resins preferably contains from 1 to 4 carbon atoms. Said aldehyde is preferably chosen from formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, 2-ethylhexanal, benzaldehyde and mixtures thereof, and more preferably from formaldehyde.

[0058] In such resins, the compounds or formula (III) are preferably chosen from those of formula (IIIa) above, wherein n ranges from 1 to 18, preferably from 1 to 15 and most preferably from 1 to 12.

[0059] Particularly preferred resins are those obtainable by condensation of at least one cardanol n EO and formaldelyde.

[0060] Preferably, said (ethoxylated) phenol compound(s) is (are) chosen from cardanol, (poly) ethoxylated cardanols chosen from cardanols n EO such as cardanol 1 EO, cardanol 2.5 EO, cardanol 5 EO, cardanol 7 EO, cardanol 12 EO, resins obtainable by condensation of at least one cardanol n EO with at least one aldehyde having from 1 to 8 carbon atoms such as formaldehyde and mixtures thereof.

[0061] Preferably, said (ethoxylated) phenol compound(s) is (are) present in an amount ranging from 0.01 to 5%wt, preferably from 0.05 to 2%wt, more preferably from 0.1 to 1%wt, relative to the total weight of the additive concentrate.

[0062] In a particular embodiment, the additive concentrate contains at least one compound chosen from cardanol, (poly) ethoxylated cardanols chosen from cardanols n EO such as cardanol 1 EO, cardanol 2.5 EO, cardanol 5 EO, cardanol 7 EO, cardanol 12 EO, resin(s) obtained by condensation of at least one cardanol n EO with at least one aldehyde having from 1 to 8 carbon atoms such as formaldehyde and mixtures thereof in an amount ranging from 0.01 to 5%wt, preferably from 0.05 to 2%wt, more preferably from 0.1 to 1%wt, relative to the total weight of the additive concentrate.

[0063] According to a preferred embodiment, the weight ratio between the total amount of (ethoxylated) phenol compound(s) on one hand and the total amount of oxazolidine compound(s) on the other hand ranges from 1:1000 to 1:100.

[0064] The additive concentrate of the invention may be mixed with a liquid solvent. Preferably, the additive concentrate of the invention is mixed with a solvent.

[0065] Therefore, another object of the invention is a composition comprising an additive concentrate as defined above and at least one liquid solvent.

Liquid solvents

[0066] By liquid, it is meant a solvent which is in liquid form at ambient temperature (20°C) and atmospheric pressure ($1{,}013.10^5$ Pa).

[0067] According to a preferred embodiment, the solvent(s) is (are) selected from organic liquid solvents.

[0068] Such solvents may in particular be chosen from poly oxyalkyl ethers, aliphatic hydrocarbons such as alkanes, aromatic solvents such as aromatic hydrocarbons and aromatic hetero-compounds, naphtas, and mixtures thereof.

[0069] Preferred organic solvents are chosen from aromatic solvents, such as N-methylpyrrolidone, xylene, toluene, benzene; and poly oxyalkyl ethers such as butyl carbitol (diethylene glycol monobutyl ether); as well as mixtures thereof.

[0070] Other preferred organic solvents include those derived from biomass, such as oils of vegetable origin. A particularly preferred solvent is cashew nutshell liquid, also known as CSNL, which is a widely available vegetable oil derived from cashew nut shell. CNSL can be used as a mixture with any other solvent such as those described herein.

[0071] The choice of the solvent mainly depends on the final use of the composition. When the composition is intended to be used for scavenging hydrogen sulphide and/or sulfhydryl-containing compounds in an aqueous stream, an organic solvent soluble in water may be preferred. When the composition is intended to be used for scavenging hydrogen sulphide and/or sulfhydryl-containing compounds in a hydrocarbon stream, an organic solvent will be preferred.

[0072] When the stream is a mixture of water and hydrocarbons (such as a mixture of crude oil and brine) a solvent having a dual solubility, i.e. a water solubility and a solubility in hydrocarbons, can be preferred. Poly alkyl ethers such as butyl carbitol are preferred solvents since they have such a dual solubility.

[0073] The composition of the invention advantageously contains an amount of solvent ranging from 1 to 50% by weight, preferably from 5 to 40%wt, more preferably from 10 to 35%wt, relative to the total weight of the composition.

[0074] The composition of the invention advantageously contains an amount of the additive concentrate of the invention ranging from 50 to 99% by weight, preferably from 55 to 90%wt, more preferably from 60 to 80%wt, relative to the total weight of the composition.

[0075] According to an embodiment of the invention, the composition comprises, preferably consists of:

- from 50 to 95%wt, preferably from 60 to 90%wt, more preferably from 70 to 80%wt, of mono-oxazolidines, bisoxazolidines and mixtures thereof,
- from 0.01 to 5%wt, preferably from 0.05 to 2%wt, more preferably from 0.1 to 1%wt, of (ethoxylated) phenol compound(s) of formula (III),
- from 1 to 50%wt, preferably from 5 to 40%wt, more preferably from 10 to 35%wt of solvent(s),

relative to the total weight of the composition.

Defoamer

[0076] The composition of the invention (ie the composition comprising the concentrate additive and the solvent) may further comprise art least one defoamer, preferably at least one silicone-based defoamer.

[0077] The defoamers are preferably chosen from polydimethylsiloxane polymers, more preferably from grafted polydimethylsiloxane polymers.

[0078] The composition of the invention advantageously contains an amount of defoamer ranging from 0.1 to 2% by weight, relative to the total weight of the composition.

Use

[0079] The present invention also encompasses the use of an additive concentrate or of a composition as described above for scavenging hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group in a liquid or gaseous stream.

[0080] The organic compounds comprising at least one sulfhydryl group are especially chosen from mercaptans, thiocarboxylic acids and dithiocarboxylic acids.

[0081] The liquid or gaseous stream may be a monophasic stream such as in particular an aqueous stream or an organic stream, or a multiphasic stream containing both water and hydrocarbons (such as for instance oil/water or oil/water/gas or gas/water).

[0082] According to a preferred embodiment, the additive concentrate and the composition of the invention are used for scavenging hydrogen sulphide (H_2S) and mercaptans (compounds of formula RSH) in a hydrocarbon containing stream.

[0083] The mercaptans which are eliminated are typically those of formula RSH wherein R is an alkyl or alkenyl group containing from 1 to 8, preferably from 1 to 6 and more preferably from 1 to 4 carbon atoms.

[0084] The hydrocarbon containing streams are typically selected from crude petroleum oils, hydrocarbon fractions and residues deriving from the distillation thereof, light petroleum gas (LPG) and natural gas, as well as mixtures thereof with aqueous phases such as brine.

[0085] Such streams contain H_2S and/or mercaptans in total amounts which may range for example from 1 to 10 000 ppm by weight.

[0086] The present invention also concerns the use of (ethoxylated) phenol compound(s) of formula (III) as defined above for improving the efficiency of an oxazolidine compound for scavenging hydrogen sulphide (H_2S) and/or mercaptans in hydrocarbon streams.

Method

[0087] The present invention also relates to a method for scavenging hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group such as mercaptans in a liquid or gaseous stream comprising contacting said stream with the additive concentrate or with the composition of the invention.

[0088] As described above, the liquid or gaseous stream may be monophasic such as in particular an aqueous stream or an organic stream, or multiphasic such as a stream containing both water and hydrocarbons (such as for instance oil/water or oil/water/gas or gas/water).

[0089] According to a preferred embodiment, the stream contains hydrocarbons. The stream may be especially selected from crude petroleum oils, hydrocarbon fractions and residues deriving from the distillation thereof such as in particular fuel oils and heavy fuel oils, light petroleum gas (LPG) and natural gas, as well as mixtures thereof with aqueous compositions such as brine.

[0090] The amount of additive concentrate or composition used per amount of stream depends on the concentration of said oxazolidine compound(s) and of (ethoxylated) phenol compound(s) of formula (III) as defined above in the composition as well as the total content of hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group in the liquid or gaseous stream, as explained above.

[0091] The concentrate or the composition is contacted with the liquid or gaseous stream for a time sufficient to achieve an effective scavenging of hydrogen sulphide and of organic compounds comprising at least one sulfhydryl group.

[0092] The example hereafter only aims at illustrating the present invention, and shall not be interpreted so as to limit its scope.

Examples

Compositions

[0093] Compositions A1 to A12 (according to the invention) and C1 (comparative) were prepared by mixing ingredients as detailed in Table 1 and Table 2 below:

Table 1

	A1	A2	A3	A4	A5	A6
MBO	70	70	70	70	70	70
Cardanol	0.5	0.25	0.1	-	-	-
Cardanol ethoxylated 7 EO	-	-	-	0.5	0.25	0.1
Butyl carbitol	29.5	29.75	29.90	29.5	29.75	29.90

Table 2

	A7	A8	A9	A10	A11	A12	C1
MBO	70	70	70	70	70	70	70

(continued)

	A7	A8	A9	A10	A11	A12	C1
Cardanol ethoxylated 9 EO	0.5	0.25	0.1	-	-	-	-
Cardanol ethoxylated 12 EO	-	-	-	0.5	0.25	0.1	-
Butyl carbitol	29.5	29.75	29.90	29.5	29.75	29.90	30

Assessment of H_2S scavenging ability

[0094] The test was carried out at room temperature. A 250 mL glass purger was charged with 100 mL of an inert solvent. A gas consisting of N_2 containing H_2S at a concentration of 50 ppm was released by a bubbling tube at a flow rate of 0.4 mL/min into the solvent contained in said purger. The solvent was continuously agitated by using a magnetic stirrer. The gas exiting the solvent and leaving the purger was conveyed to a H_2S detector.

[0095] At the beginning of each test, a setup was made as follows: the gas (H_2S in N_2 at a concentration of 50 ppm) was passed through the purger with a 0.4 mL/min flow rate, and the H_2S detector started recording the H_2S concentration at the outlet of the purger. Once the outlet H_2S concentration remained stable (with a value of 50 ppm constant reading at the detector), the scavenging composition (1ml of said composition is mixed with 2ml of butyl carbitol to ensure proper injection into the reactor) to be tested was quickly injected into the purger. As the scavenging composition starts reacting with H_2S which results in a reduction of the H_2S concentration at the outlet, as recorded by the detector. The H_2S concentration was recorded at every 5 sec time interval.

[0096] An interval of time of 30 min was respected between each test. In each test, once the H_2S scavenger has been injected into the purger, the concentration of H_2S recorded by the detector started decreasing from 50 ppm down to towards 0 ppm, depending on the efficiency of the scavenging composition. The higher the H_2S scavenging efficiency of the composition, the faster the H_2S concentration recorded by the detector drops and the longer the rate of H_2S concentration recorded by the detector remains low. It was also observed that, once the scavenging composition was consumed, the concentration of H_2S recorded by the detector started increasing slowly back to 50 ppm.

Results

[0097] The results obtained are detailed in the Table below:

Tested composition	Max H2S Scavenging Obtained (in %)	Time required to achieve max H2S scavenging (in sec)	H2S Scavenging Obtained (in %) at the end of the test (1800 sec)
A1	100	120	100
A2	96	120	85
A3	94	120	79
A4	82	120	65
A5	84	120	65
A6	92	120	68
A7	86	120	62
A8	88	120	64
A9	90	120	64
A10	76	130	62
A11	84	120	64
A12	100	120	70
C1	56	190	16

[0098] The results show that the compositions A1-A12 according to the invention are more efficient in scavenging H_2S than comparative composition C1 comprising MBO only. Indeed, the percentage of maximum H_2S scavenging is higher

and obtained in much less time with the compositions A1-A12. Moreover, the scavenging effect is longer in time, as at the end of the test, the percentage of scavenging obtained with the compositions of the invention is still much higher than with the comparative composition C1.

Claims

1. Additive concentrate comprising at least one oxazolidine compound and at least one (ethoxylated) phenol compound chosen from compounds having the following formula (III):

$$R\text{-}Ph\text{-}(OCH_2CH_2)_n\text{-}OH \qquad (III)$$

wherein

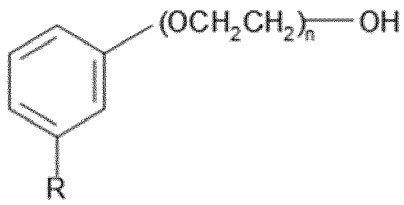
Ph denotes a benzene ring,
R represents a linear or branched saturated or unsaturated hydrocarbon chain comprising from 8 to 24 carbon atoms, which may be substituted or not substituted, and
n represents a number ranging from 0 to 20,
and from derivatives of such compounds of formula (III).

2. Additive concentrate as defined in claim 1, wherein the oxazolidine compound(s) is (are) chosen from compounds comprising one oxazolidine cycle (i.e. mono-oxazolidines) or two oxazolidine cycles (i.e. bisoxazolidines), preferably from 1,3-oxazolidine, 5-methyloxazolidine, 3-(C1-C20)alkyl-oxazolidines, 3,3'-methylenebis(oxazolidine), 3,3'-methylenebis(5-methyloxazolidine) (MBO) and mixtures thereof.

3. Additive concentrate as defined in any preceding claim, wherein the oxazolidine compound(s) is (are) present in an amount ranging from 60 to 80% by weight, preferably from 95 to 99.99%wt, preferably from 98 to 99.95%wt, more preferably from 99 to 99.90%wt, relative to the total weight of the additive concentrate.

4. Additive concentrate as defined in any preceding claim, wherein (ethoxylated) phenol compound are chosen from compounds of formula (III) wherein R represents a linear or branched saturated or unsaturated hydrocarbon group comprising from 8 to 24 carbon atoms, preferably from 10 to 22 carbon atoms, even more preferably from 12 to 14 carbon atoms.

5. Additive concentrate as defined in any preceding claim, wherein the compounds of formula (III) are chosen from those having developed formula (IIIa) below:



(IIIa)

wherein R is defined as in anyone of claim 1 or 4 and n is defined as in claim 1.

6. Additive concentrate as defined in anyone of claims 1 to 4, wherein the (ethoxylated) phenol compound(s) are chosen from resins obtainable by condensation of at least one compound of formula (III), with at least one aldehyde having from 1 to 8 carbon atoms, preferably from resins obtainable by condensation of at least one compound of formula (IIIa) wherein n ranges from 1 to 18, preferably from 1 to 15 and most preferably from 1 to 12 and of formaldehyde.

7. Additive concentrate as defined in any preceding claim, wherein the (ethoxylated) phenol compound(s) is (are) present in an amount ranging from 0.01 to 5%wt, preferably from 0.05 to 2%wt, more preferably from 0.1 to 1%wt, relative to the total weight of the additive concentrate.

8. Additive concentrate as defined in any preceding claim, wherein the weight ratio between the total amount of (ethoxylated) phenol compound(s) on one hand and the total amount of oxazolidine compound(s) on the other hand ranges from 1:1000 to 1:100.

9. Composition comprising an additive concentrate as defined in any preceding claim and at least one liquid solvent, preferably chosen from organic solvents, more preferably from aromatic solvents, poly oxyalkyl ethers, naphtas and organic solvents derived from biomass, more preferably from oils of vegetable origin, and even more preferably from cashew nutshell liquid and mixtures thereof with other organic solvents.

10. Composition as defined in the preceding claim, wherein the solvent(s) is (are) present in an amount ranging from 1 to 50% by weight, preferably from 5 to 40%wt, more preferably from 10 to 35%wt, relative to the total weight of the composition.

11. Composition as defined in anyone of claims 9 and 10, wherein the additive concentrate is present in an amount ranging from 50 to 99% by weight, preferably from 55 to 90%wt, more preferably from 60 to 80%wt, relative to the total weight of the composition.

12. Composition as defined in anyone of claims 9 to 11 further comprising at least one defoamer, preferably chosen from polydimethylsiloxane polymers, more preferably from grafted polydimethylsiloxane polymers.

13. Use of an additive concentrate as defined in anyone of claims 1 to 8 or of a composition as defined in anyone of claims 9 to 12 for scavenging hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group such as mercaptans in a liquid or gaseous stream.

14. Use of (ethoxylated) phenol compounds as defined in anyone of claims 1 and 4 to 7 for improving the efficiency of an oxazolidine compound for scavenging hydrogen sulphide (H_2S) and/or organic compounds comprising at least one sulfhydryl group such as mercaptans in a liquid or gaseous stream, preferably in a hydrocarbon streams.

15. Method for scavenging hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group such as mercaptans in a liquid or gaseous stream, comprising contacting said stream with an additive concentrate as defined in anyone of claims 1 to 8 or with a composition as defined in anyone of claims 9 to 12.

Amended claims in accordance with Rule 137(2) EPC.

1. Additive concentrate comprising at least one oxazolidine compound and at least one (ethoxylated) phenol compound chosen from compounds having the following formula (III):

$$R\text{-}Ph\text{-}(OCH_2CH_2)_n\text{-}OH \qquad (III)$$

wherein

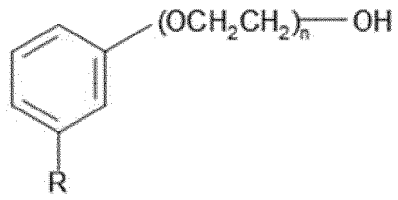
Ph denotes a benzene ring,
R represents a linear or branched saturated or unsaturated hydrocarbon chain comprising from 8 to 24 carbon atoms, which may be substituted or not substituted, and
n represents a number ranging from 0 to 20,
wherein the weight ratio between the total amount of (ethoxylated) phenol compound(s) on one hand and the total amount of oxazolidine compound(s) on the other hand ranges from 1:1000 to 1:100.

2. Additive concentrate as defined in claim 1, wherein the oxazolidine compound(s) is (are) chosen from compounds comprising one oxazolidine cycle (i.e. mono-oxazolidines) or two oxazolidine cycles (i.e. bisoxazolidines), preferably from 1,3-oxazolidine, 5-methyloxazolidine, 3-(C1-C20)alkyl-oxazolidines, 3,3'-methylenebis(oxazolidine), 3,3'-methylenebis(5-methyloxazolidine) (MBO) and mixtures thereof.

3. Additive concentrate as defined in any preceding claim, wherein the oxazolidine compound(s) is (are) present in an amount ranging from 60 to 80% by weight, preferably from 95 to 99.99%wt, preferably from 98 to 99.95%wt, more preferably from 99 to 99.90%wt, relative to the total weight of the additive concentrate.

4. Additive concentrate as defined in any preceding claim, wherein (ethoxylated) phenol compound are chosen from compounds of formula (III) wherein R represents a linear or branched saturated or unsaturated hydrocarbon group comprising from 8 to 24 carbon atoms, preferably from 10 to 22 carbon atoms, even more preferably from 12 to 14 carbon atoms.

5. Additive concentrate as defined in any preceding claim, wherein the compounds of formula (III) are chosen from those having developed formula (IIIa) below:



(IIIa)

wherein R is defined as in anyone of claim 1 or 4 and n is defined as in claim 1.

6. Additive concentrate as defined in any preceding claim, wherein the (ethoxylated) phenol compound(s) is (are) present in an amount ranging from 0.01 to 5%wt, preferably from 0.05 to 2%wt, more preferably from 0.1 to 1%wt, relative to the total weight of the additive concentrate.

7. Composition comprising an additive concentrate as defined in any preceding claim and at least one liquid solvent, preferably chosen from organic solvents, more preferably from aromatic solvents, poly oxyalkyl ethers, naphtas and organic solvents derived from biomass, more preferably from oils of vegetable origin, and even more preferably from cashew nutshell liquid and mixtures thereof with other organic solvents.

8. Composition as defined in the preceding claim, wherein the solvent(s) is (are) present in an amount ranging from 1 to 50% by weight, preferably from 5 to 40%wt, more preferably from 10 to 35%wt, relative to the total weight of the composition.

9. Composition as defined in anyone of claims 7 and 8, wherein the additive concentrate is present in an amount ranging from 50 to 99% by weight, preferably from 55 to 90%wt, more preferably from 60 to 80%wt, relative to the total weight of the composition.

10. Composition as defined in anyone of claims 7 to 9 further comprising at least one defoamer, preferably chosen from polydimethylsiloxane polymers, more preferably from grafted polydimethylsiloxane polymers.

11. Use of an additive concentrate as defined in anyone of claims 1 to 6 or of a composition as defined in anyone of claims 7 to 10 for scavenging hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group such as mercaptans in a liquid or gaseous stream.

12. Use of (ethoxylated) phenol compounds as defined in anyone of claims 1 and 4 to 6 for improving the efficiency of an oxazolidine compound for scavenging hydrogen sulphide (H_2S) and/or organic compounds comprising at least one sulfhydryl group such as mercaptans in a liquid or gaseous stream, preferably in a hydrocarbon streams.

13. Method for scavenging hydrogen sulphide and/or organic compounds comprising at least one sulfhydryl group such as mercaptans in a liquid or gaseous stream, comprising contacting said stream with an additive concentrate as defined in anyone of claims 1 to 6 or with a composition as defined in anyone of claims 7 to 10.

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EUROPEAN SEARCH REPORT

Application Number
EP 23 30 5517

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2018/179432 A1 (BAO XIAOYING [US] ET AL) 28 June 2018 (2018-06-28) * example 8 *	1,2,4,5,9	INV. C10L1/10 C10G75/00 C10L1/14
X	US 2022/025285 A1 (MONDKAR HEMANT SURENDRA [IN] ET AL) 27 January 2022 (2022-01-27) * paragraphs [0056], [0098], [0104]; claim 1; example 2 *	1-15	

TECHNICAL FIELDS SEARCHED (IPC)

C10L
C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	13 September 2023	Klaes, Daphne

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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13-09-2023

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- WO 2017102693 A **[0012]**