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(56) Documents Cited

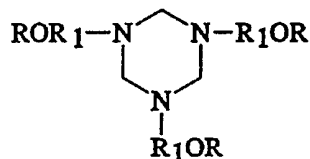
WO 94/08980 A1 US 3791974 A

(58) Field of Search

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(54) **Preparation of hexhydrotriazine compounds and their use in removing hydrogen sulphide from hydrocarbon fluids**

(57) A method of removing H₂S and/or mercaptans from a fluid which comprises contacting the fluid with an effective amount of a hexahydrotriazine of formula:



in which R is an alkyl group having from 1 to 6 carbon atoms; and R₁ is an alkylene group having 2 to 5 carbon atoms, which has been prepared by reacting an appropriate alkoxy-alkylamine with formaldehyde, formalin or paraformaldehyde.

GB 2 290 542 A

METHOD OF TREATING SOUR GAS
AND LIQUID HYDROCARBONBACKGROUND OF THE INVENTION

This invention relates generally to the treatment of sour gas and liquid hydrocarbon to remove or reduce the levels of hydrogen sulfide therein. In one aspect, the invention relates to the treatment of sour gas and oil streams flowing in a flow line. In another aspect, the invention relates to the use of nonregenerative scavengers to reduce the levels of hydrogen sulfide in natural gas and liquid hydrocarbons. In still another aspect, the invention relates to the use of a hexahydro-triazine as an H₂S scavenger for oil field produced fluids.

The toxicity of hydrogen sulfide in hydrocarbon streams is well known in the industry and considerable expense and efforts are expended annually to reduce its content to a safe level. Many regulations require pipeline gas to contain no more than 4 ppm hydrogen sulfide.

In large production facilities, it is generally more economical to install a regenerative system for treating sour gas streams. These systems typically employ a compound used in an absorption tower to contact the produced fluids and selectively absorb the hydrogen sulfide and possibly other toxic materials such as carbon dioxide and mercaptans. The absorption compound is then regenerated and reused in the

system. Typical hydrogen sulfide absorption materials include alkanolamines, PEG, hindered amines, and the like.

However, during a development stage of a field or in small producing fields where regenerative systems are not economical, it is necessary to treat the sour hydrocarbon production with nonregenerative scavengers.

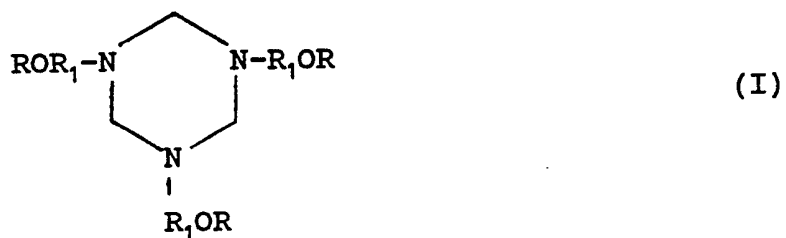
Based on an article appearing in the Oil & Gas Journal, January 30, 1989, nonregenerative scavengers for small plant hydrogen sulfide removal fall into four groups: aldehyde based, metallic oxide based, caustic based, and other processes. In the removal of hydrogen sulfide by nonregenerative compounds, the scavenger reacts with the hydrogen sulfide to form a nontoxic compound or a compound which can be removed from the hydrocarbon. For example, in the formaldehyde type reaction, the reaction produces a chemical complex known as formthionals (e.g., trithiane).

As described in detail below, the present invention employs a nonregenerative scavenger which may be of the aldehyde type. These include low molecular weight aldehydes and ketones and adducts thereof. The low molecular weight aldehydes may also be combined with an alkyl or alkanolamine as disclosed in U.S. Patent 4,748,011. Other aldehyde derived scavengers include the reaction product of low molecular weight alkanolamines and aldehydes disclosed in U.S. Patent 4,978,512. PCT Application WO 92/01481 discloses a method of reducing sulphides in a sewage gas using certain tri-substi-

tuted-hexahydro-s-triazines. German reference DE4027300 discloses a regenerative solvent for removing H₂S and mercaptans. The solvent is a heterocyclic compound (e.g. a 1,3,5-trimethyl-1,3,5-triazine).

SUMMARY OF THE INVENTION

In accordance with the method of the present invention, sour produced fluid such as H₂S sour gas or liquid hydrocarbons are treated with 1,3,5-tri-substituted-hexahydro-1,3,5-triazine to reduce the level of H₂S and mercaptans therein. The substituted-hexahydro-triazine may be 1,3,5-trialkoxyalkyl-hexahydro-1,3,5-triazines wherein the alkoxy group contains from 1 to 5 carbon atoms and the alkyl group contains from 2 to 6 carbon atoms having the following formula:



where

R is an alkyl group having from 1 to 6 carbon atoms,
preferably 1;

R₁ is an alkyl group having 2 to 5 carbon atoms,
preferably 2 to 3 carbon atoms.

The substituted-hexahydro-triazine may be manufactured by reacting an alkoxyalkyl amine with formalin or a lower

aldehyde such as formaldehyde to form an aqueous solution of the hexahydro-triazine. The water is then distilled off leaving the hexahydro-triazine which can be used in neat form or dissolved in a suitable solvent. It has surprisingly been discovered that the hexahydro-triazine described above is soluble (up to at least 20% by weight) in a variety of liquids, ranging from water base to oil base. The significance of the solubility is that it can be selectively tailored to treat oil systems with water or oil systems substantially free of water as in refined products.

The preferred hexahydro-triazine is 1,3,5-trimethoxypropyl-hexahydro-1,3,5-triazine (MOPA hexahydro-triazine).

The MOPA hexahydro-triazine is prepared by reacting methoxypropyl amine with formalin or a lower aldehyde such as formaldehyde. In one embodiment, the hexahydro-triazine scavenger can be used as manufactured (water solution). For use in oil base formulations, the scavenger can be used in neat form or dissolved in a suitable solvent.

The method of the present invention involves adding the hexahydro-triazine scavenger described above to any gas or liquid hydrocarbon containing H_2S and/or mercaptans in a sufficient quantity to effectively reduce the levels of reactive S therein. The method may also be employed by passing the sour gas through an absorption tower containing a solution of the scavenger. Because of its solubility in oil

the scavenger is preferably substantially water free and is used in substantially water free systems.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of the present invention may be used in the treatment of sour gas and oil production streams, as well as in petroleum (e.g. crude oil and refined products) contained in storage tanks, vessels, pipelines. etc.

As mentioned above, the scavenging composition useful in the method of the present invention is 1,3,5-tri-substituted hexahydro-1,3,5-triazine. (For convenience, this compound is referred to herein as "hexahydro-triazine", unless otherwise indicated to distinguish between other triazines.) The preferred hexahydro-triazine may be prepared by the condensation reaction of a methoxypropylamine (MOPA) with formaldehyde or other lower aldehyde to yield the MOPA Hexahydro-Triazine.

The formaldehyde may be in the form of formalin or para-formaldehyde, with the former being preferred.

Although the preferred hexahydro-triazine is the MOPA Hexahydro-Triazine, other hexahydro-triazines within the scope of Formula I include 1,3,5-tri-methoxyethyl-hexahydro-1,3,5-triazine (from 2-methoxyethyl amine); 1,3,5-tri-(3-ethoxypropyl)-hexahydro-1,3,5-triazine (from 3-ethoxypropylamine); 1,3,5-tri-(3-isopropoxypropyl)-hexahydro-1,3,5-triazine (from 3-ethoxypropylamine); 1,3,5-tri-(3-butoxy-

propyl)-hexahydro-1,3,5-triazine (from 3-butoxypropylamine); 1,3,5-tri-(3-butoxypropyl)-hexahydro-1,3,5-triazine (from 3-butoxypropylamine); and 1,3,5-tri-(5-methoxypentyl)-hexahydro-1,3,5-triazine (from 5-methoxypentylamine).

In carrying out the reaction to make the preferred hexahydro-triazine, MOPA is added slowly to a concentrated aqueous solution of formaldehyde and the stoichiometry is maintained so that there is an exact equivalent to a slight excess of the amine at the end of the reaction, maintaining a molar ratio of at least 1.00 to 1.02 moles of the amine to 1.00 moles of formaldehyde for the overall process. Free formaldehyde is minimized to <1000 ppm in the liquid. Slow addition is desirable to control the reaction temperature to below 140°F. For climatization purposes, methanol or other solvents can be added back without adversely affecting the formaldehyde level. Thus, an essentially quantitative yield of 1,3,5-(tri-methoxypropyl) hexahydro-1,3,5-triazine can be formed under conditions which minimize the presence of objectionable amounts of free formaldehyde.

The hexahydro-triazine may also be manufactured by the reverse addition of formaldehyde or paraformaldehyde to the MOPA to produce the same result, provided the temperature is maintained below 140°F and provided the stoichiometry of the overall process is as described above.

Although the MOPA Hexahydro-Triazine can be used as an aqueous solution as produced, it is preferred to distill off

the water to produce a neat product, which can be used in that form or mixed with a mutual solvent such as alcohols, ethylene glycol monobutyl ether, or an oil solvent such as heavy aromatic naphthene, alkanes, aromatics, etc. The mutual solvent with the hexahydro-triazine offers the versatility of using the scavenger with either oil or water systems. The concentration of the hexahydro-triazine in the solvent may vary within wide ranges from 5 to 95 wt%, with 25 to 75 wt% being preferred.

The preferred oil solvents are chosen on the basis of the intended application. For example, kerosene and heavy aromatic naphtha offer advantages for carrier solvents to treat oil systems. High boiling process hydrocarbon solvents offer advantage as a carrier to treat higher temperature asphalt materials.

Operations

In carrying out the method of the present invention, the scavenging composition is added to the water or oil stream in a concentration sufficient to substantially reduce the levels of H₂S and/or mercaptans therein. In gas, generally from 0.01 to 0.12, preferably from 0.02 to 0.10, most preferably from 0.04 to 0.08 gallons of scavenger product (100% active) per MMSCF for each ppm of H₂S removed will be sufficient for most applications. The treatment may also be based on weight of H₂S in the gas. From 1 to 50, preferably 2 to 20 pounds and

most preferably from 4 to 10 pounds of hexahydro-triazine per pound of H₂S removed will normally be required.

In treating hydrocarbon streams, the scavenging compound contained in a solvent, such as a mutual solvent or aromatic solvent, may be injected by conventional means such as a chemical injection pump or any other mechanical means for dispersing chemicals in the stream. The injection may be in the flow lines or the gas may be passed through an absorption tower containing a solution of the hexahydro-triazine.

For sour oil from 1 to 50 pounds, preferably from 2 to 20 pounds, and most preferably from 4 to 10 pounds of hexahydro-triazine per pound of H₂S removed will be sufficient.

In addition to the hexahydro-triazines described above, the chemical formulations may also contain other compounds such as ethoxylated alcohols, ethoxylated phenols, sulfates of ethoxylated alcohols and phenols, quaternary amines, corrosion inhibitors, and the like. The most preferred scavenger formulation comprises 25-75 wt% actives (hexahydro-triazines). The 100% wt% active (hexahydro-triazine) can be successfully used as is without formulation.

The H₂S scavenging ability of the hexahydro-triazine is believed to be due to its reaction with hydrogen sulfide to produce sulfur containing organic compounds such as dithiazines.

EXPERIMENTS

Preparation of Scavenger

The MOPA Hexahydro-Triazine scavenger useful in the method of the present invention was prepared as follows:

A stainless steel 1-liter reactor was charged with 476.56 gr. of formalin solution (37% active formaldehyde) and 523.44 gr. of methoxypropylamine was slowly added over a period of about 15 minutes. The reaction exotherm was controlled with an ice bath. The reaction temperature was maintained between 56°C to 68°C. When methoxypropylamine addition was complete, the reaction mixture was heated to remove water and methanol (from formalin) by distillation. The distillation was terminated as the reaction mixture approached 150°C. The reactor contents were then rapidly cooled to room temperature. A yield of 583 grams of triazine was obtained, which was light in color. Subsequent preparations have established that the preferred reaction temperature is 50°C to 60°C and that the preferred cutoff temperature for the distillation is a pot temperature of 130°C. The scavenger referred to herein as MOPA Hexahydro-Triazine was tested in neat form.

Tests of Scavenger (Examples):

Example 1:

A hydrogen sulfide scavenging test was conducted by partially saturating kerosene with H₂S gas at room temperature. Bottle 1 contained no scavenger. The scavenger,

prepared as described above, was added in neat form to bottle 2. A commercial aldehyde type scavenger (designated Commercial A) was added to bottle 3. The bottles were shaken and the concentration of H₂S in the vapor phase of each bottle was measured with elapsed time (at room temperature). The data are presented in TABLE I.

TABLE I

<u>Bottle</u>	<u>Scavenger</u>	<u>Amount (cc)</u>	<u>H₂S Contained in Vapor Phase</u>			
			<u>Elapsed time (hr.):</u>	<u>1.5</u>	<u>24</u>	<u>90</u>
1	None	-		1.10%	1.0%	1.55%
2	MOPA Hexahydro- Triazine	1.0		1.05%	0.13%	0%
3	Commercial A	1.0		1.09%	1.00%	0.92%

The above test in kerosene demonstrates that the MOPA Hexahydro-Triazine scavenger is effective in oil, whereas the commercial aldehyde scavenger was not effective.

Example 2:

A 50% solution of MOPA Hexahydro-Triazine was prepared by dissolving 50 wt% MOPA Hexahydro-Triazine in 50 wt% ethylene glycol monobutyl ether. This is designated 50% Formula. This formulation was tested versus a commercial H₂S scavenger which is designated commercial U. In these tests the kerosene was more thoroughly saturated with H₂S than the Example 1 tests. The results are shown in TABLE II.

TABLE II

<u>Bottle</u>	<u>Scavenger</u>	<u>Amount (cc)</u>	<u>H₂S Contained in Vapor Phase</u>			
			<u>Elapsed time (hr.):</u>	<u>20</u>	<u>44</u>	<u>60</u>
1	None	-		8.4%	8.3%	8.0%
2	50% Formula	3.0		5.0%	0.3%	0.0%
3	Commercial U	3.0		2.8%	2.2%	1.8%

This test illustrates excellent H₂S removing capacity for the MOPA Hexahydro-Triazine in simple 50% formulation form.

Example 3:

The Example 3 tests were the same as the Example 2 tests, except the bottles contained kerosene of slightly less H₂S saturation than the bottles in Example 2 tests.

TABLE III

Bottle	Scavenger	Amount (cc)	H ₂ S Contained in Vapor Phase			
			Elapsed time (hr.):	17	46	114
1	None	-		6.8%	6.4%	6.9%
2	50% Formula	2.5		3.7%	480 ppm	0

These tests collectively show the ability of the MOPA Hexahydro-Triazine to effectively reduce the concentration of H₂S to zero.

Example 4:

To demonstrate the solubility of the MOPA Hexahydro-Triazine in a variety of liquids, the following tests were conducted. A 5 cc sample of the scavenger was mixed with a 20 cc sample of a liquid in a bottle and the bottle was vigorously shaken five times. The qualitative data are shown in TABLE IV.

TABLE IV

Fluid	Scavenger			
	MOPA HexahydroTriazine	Ethanol Amine Hexahydro- Triazine Concentrate	Commercial Triazine B	Commercial Triazine C
Water	Soluble	Soluble	Soluble	Soluble
Methanol	Soluble	Soluble	Soluble	Soluble
Isopropanol	Soluble	Soluble	Soluble	Soluble

TABLE IV
(continued)

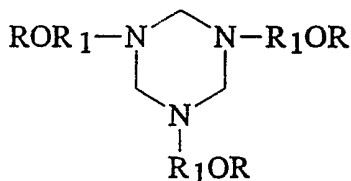
Fluid	Scavenger		Commercial Triazine - B	Commercial Triazine - C
	MOPA HexahydroTriazine	Ethanol Amine Hexahydro- Triazine Concentrate		
Ethylene Glycol Monobutyl Ether	Soluble	Soluble	Soluble	Soluble
Kerosene	Soluble	Insoluble	Insoluble	Insoluble
Diesel	Soluble	Insoluble	Insoluble	Insoluble
Paraffinic Oil	Soluble	Insoluble	Insoluble	Insoluble
Xylene	Soluble	Insoluble	Insoluble	Insoluble
Heavy Aromatic Naphtha	Soluble	Insoluble	Insoluble	Insoluble

As shown in TABLE IV, it was surprisingly discovered that the MOPA triazine is soluble in a variety of diverse solvents. The ethanol amine hexahydro-triazine concentrate was prepared by a process analogous to what was described for the MOPA Hexahydro-Triazine except that the reaction product began to discolor as the reactor was heated to remove water. The product could be concentrated, but it suffered severe discoloration and the stripping was terminated at a pot temperature of 120°F. Commercial Triazine A and Commercial Triazine B are products which have been marketed as H₂S scavengers.

The above tests demonstrate the universal solubility of the MOPA Hexahydro-Triazine and the effectiveness in treating oil. In comparison, the other triazines tested were not oil soluble, which could lead to operational problems in treating oil production and/or products: (1) the undesirability of adding water to products, and (2) dispersability.

CLAIMS

1. A method of removing H₂S and/or mercaptans from a fluid which comprises contacting the fluid with an effective amount of a hexahydrotriazine of formula:



in which R is an alkyl group having from 1 to 6 carbon atoms; and R₁ is an alkylene group having 2 to 5 carbon atoms, the hexahydrotriazine being prepared by reacting an alkoxyalkyl amine, in which the alkoxy moiety contains 1 to 6 carbon atoms and the alkyl moiety contains 2 to 5 carbon atoms, with formalin, formaldehyde or paraformaldehyde to form an aqueous solution of hexahydrotriazine and then removing water by distillation to form a substantially water-free hexahydrotriazine.

2. A method according to claim 1, wherein the alkoxyalkyl amine is methoxypropylamine and the hexahydrotriazine is 1,3,5-trimethoxypropyl-hexahydro-1,3,5-triazine.

3. A method according to claim 1 or 2, further comprising dissolving the substantially water-free hexahydrotriazine in a solvent selected from water, alcohols, hydrocarbon solvents and oxygenated solvents.

4. A method according to claim 3, wherein the solvent is selected from paraffins, aromatics, ethylene glycol monobutyl-ether and propylene glycol.

5. A method according to claim 1, wherein the hexahydrotriazine is 1,3,5-trimethoxypropyl-hexahydro-1,3,5-triazine.

6. A method according to any one of claims 1 to 5, wherein the fluid is an oil field produced fluid comprising gas, oil or a mixture thereof.

10 7. A method according to any one of claims 1 to 5, wherein the fluid is a liquid hydrocarbon.

8. A method according to claim 7, wherein the liquid hydrocarbon is contacted with from 0.45 to 22.68kg (1 to 50 pounds) of hexahydrotriazine per kg of H₂S and/or mercaptans to be removed.

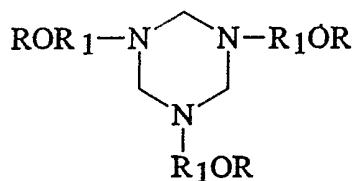
9. A method according to claim 7 or 8, wherein hexahydrotriazine is dissolved in an oil based solvent.

10. A method according to any one of claims 7 to 9, wherein the liquid hydrocarbon is substantially water free.

20 11. A method according to any one of claims 1 to 5, wherein the fluid is a gas.

12. A method according to claim 11, wherein the gas is contacted with from 0.038 to 0.454 l (0.01 to 0.12 US gallons) of hexahydrotriazine per ppm of H₂S and/or mercaptans to be removed.

13. A process for preparing a hexahydrotriazine of formula:



5

in which R is an alkyl group having from 1 to 6 carbon atoms; and

R₁ is an alkylene group having 2 to 5 carbon atoms which comprises reacting an alkoxyalkyl amine, in which the
10 alkoxy moiety contains 1 to 6 carbon atoms and the alkyl moiety contains 2 to 5 carbon atoms, with formalin, formaldehyde or paraformaldehyde, and then removing water by distillation to form a substantially water-free hexahydrotriazine.

15 14. A process according to claim 13, wherein the alkoxyalkyl amine is methoxypropylamine and the hexahydrotriazine is 1,3,5-trimethoxypropyl-hexahydro-1,3,5-triazine.

20 15. A method according to claim 1 substantially as hereinbefore described.

16. A fluid when obtained by a method as defined in any one of claims 1 to 12 or 15.

17. A process according to claim 13 substantially as hereinbefore described.

Relevant Technical Fields

(i) UK CI (Ed.N) C2C (CWH)

(ii) Int CI (Ed.6) C07D 25/04

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASE: CAS ONLINE

Search Examiner
 S I AHMAD

Date of completion of Search
 20 SEPTEMBER 1995

Documents considered relevant following a search in respect of Claims :-
 1-17

Categories of documents

- | | |
|---|---|
| X: Document indicating lack of novelty or of inventive step. | P: Document published on or after the declared priority date but before the filing date of the present application. |
| Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. | E: Patent document published on or after, but with priority date earlier than, the filing date of the present application. |
| A: Document indicating technological background and/or state of the art. | &: Member of the same patent family; corresponding document. |

Category	Identity of document and relevant passages	Relevant to claim(s)
X	WO 94/08980 A1 (BAKER HUGHES INC)	1, 13 at least
X	US 3791974 (FERRO CORPN)	13 at least

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