

USE OF ALPHA-AMINO ETHERS FOR THE REMOVAL OF HYDROGEN SULFIDE FROM HYDROCARBONS

Cross-Reference to Related Applications

None.

5 Statement Regarding Federally Sponsored Research or Development

Not Applicable.

Background 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. The toxicity of hydrogen sulfide in hydrocarbon fluids is well known in the industry. This has caused considerable
10 expense and efforts to be expended annually to reduce its content to a safe level.

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
15 compound is then regenerated and reused in the system. Typical hydrogen sulfide absorption materials include alkanolamines, PEG, hindered amines, and other species that can be regenerated.

Nonregenerative scavengers for small plant hydrogen sulfide removal fall into four
20 general categories: 1) aldehyde based, 2) metallic oxide based, 3) caustic based, and 4) other processes. In the removal of hydrogen sulfide by nonregenerative compounds, the scavenger reacts with the hydrogen sulfide to form a nonlethal compound or a compound, which can be removed from the hydrocarbon. For example, when formaldehyde reacts with hydrogen sulfide a chemical compound known as formthionals (e.g., trithiane) is formed.

Prior Art aldehyde scavengers typically 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 US Patent 4,748,011. Other aldehyde derived scavengers include the reaction product of low molecular weight alkanolamines and aldehydes as disclosed in US Patent 4,978,512. PCT Application WO 92/01481 discloses a method of reducing sulfides in different applications using certain tri-substituted-hexahydro-s-triazines. German reference DE4027300 discloses a regenerative solvent for removing H₂S and mercaptans. US Patent 5,347,004 discloses the use of 1,3,5 alkoxyalkylene hexahydro triazines. PCT Application WO 91 US 5232 discloses hydroxyalkyl triazine scavengers, specifically an N,N',N''-tris(2-hydroxyethyl)hexahydro-s-triazine. US Patent 5,774,024 discloses the combination of an alkyl triazine scavenger and quaternary ammonium salt, where the quaternary ammonium salt enhances the effectiveness of the alkyl-triazine.. These prior art attempts however are frequently water-based chemicals and require significant mixing to allow the scavenger to effectively contact the hydrocarbon fluid and remove the hydrogen sulfide.

Thus there is clear need and utility for an improved method of scavenging hydrogen sulfide from hydrocarbon fluids using scavengers that are soluble in the fluid that is being treated. The art described in this section is not intended to constitute an admission that any patent, publication or other information referred to herein is "prior art" with respect to this invention, unless specifically designated as such. In addition, this section should not be construed to mean that a search has been made or that no other pertinent information as defined in 37 CFR § 1.56(a) exists.

Brief Summary of the Invention

At least one embodiment of the invention is directed towards a method for

removing hydrogen sulfide from a hydrocarbon fluid. The method comprises contacting the fluid with an effective amount of a composition comprising a hydrogen sulfide scavenger. The amount of hydrogen sulfide scavenger is sufficient to react with the hydrogen sulfide to reduce the amount hydrogen sulfide released into the vapor space. The reaction product of the hydrogen sulfide scavenger and the hydrogen sulfide remain soluble in the hydrocarbon fluid. The hydrogen sulfide scavenger contains at least one alpha-amino ether.

The composition may include one item selected from the list consisting of:

N,N'-oxybis(methylene)bis(N,N-dibutylamine),

N,N'-(methylenebis(oxy)bis(methylene))bis(N,N-dibutylamine),

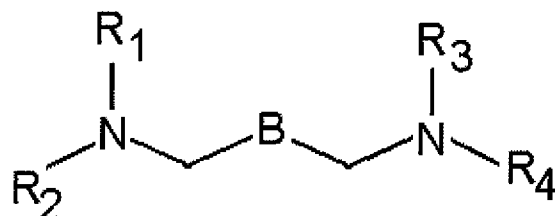
and any combination thereof.

The reaction product of the sulfide scavenging formulation and the hydrogen sulfide may not form a separate fluid layer. The method may also further comprise the step of reacting a secondary amine with a formaldehyde equivalent to form at least some of the scavenging formulation. The hydrocarbon fluid may be a liquid.

Detailed Description of the Invention

For purposes of this application the definition of these terms is as follows:

"Alpha-amino ether" means a molecule according to the formula:



Where: R₁, R₂, R₃, R₄, are carbon containing side chains containing 1 – 20 carbon atoms and includes cyclic and acyclic compounds. The cyclic compounds can be aromatic or non-aromatic.

Examples include but are not limited to, methyl, ethyl, propyl, tert-butyl, cyclopentyl, cyclohexyl, morpholino, and phenyl, and they all can be the same group or one or more different groups. B is an ether group, which is either an oxygen atom or a group having an oxygen atom at both ends (such as $-\text{OCH}_2\text{O}-$ or $-\text{OC}_2\text{H}_4\text{O}-$).

5 “Formaldehyde equivalent” means a composition of matter containing at least one group according to the formula: $(\text{CH}_2\text{O})_n$ in which n is an integer greater than or equal to 1, and/or a composition of matter including formaldehyde or related molecules such as paraformaldehyde, and/or s-trioxane.

 “Hydrocarbon fluid” means a liquid or gas predominantly comprising organic
10 material including but not limited to kerosene, crude oil, crude oil emulsions, oilfield condensate, petroleum residua, refined fuels, distillate fuels, fuel oil, heating oils, diesel fuel, gasoline, jet fuel, bunker fuel oils, and any combination thereof.

 “Non-Regenerative Scavenger” means a scavenger, which is consumed by the process of scavenging.

15 “Regenerative Scavenger” means a scavenger, which is not consumed by the process of scavenging.

 “Scavenger” means a composition of matter, such as but not limited to alpha-amino ethers, useful in reducing the amount of or mitigating the effects of some other composition of matter, such as but not limited to hydrogen sulfide, in a fluid medium.

20 In the event that the above definitions or a description stated elsewhere in this application is inconsistent with a meaning (explicit or implicit) which is commonly used, in a dictionary, or stated in a source incorporated by reference into this application, the application and the claim terms in particular are understood to be construed according to the definition or description in this application, and not according to the common definition, dictionary definition,

or the definition that was incorporated by reference. In light of the above, in the event that a term can only be understood if it is construed by a dictionary, if the term is defined by the *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th Edition, (2005), (Published by Wiley, John & Sons, Inc.) this definition shall control how the term is to be defined in the claims.

5 In at least one embodiment, the hydrogen sulfide in a hydrocarbon fluid is reduced by the introduction of an alpha-amino ether scavenger into the fluid.

 In at least one embodiment the alpha-amino ether is a portion of a scavenging formulation is used in a hydrocarbon fluid. The formulation comprises alpha-amino ether and can consist of a carrier liquid as well. The formulation can be introduced into the hydrocarbon
10 fluid by mechanical means including but not limited to injection pumps or any mechanism disclosed in US Patents 5,744,024 and 5,840,177. In the context of gaseous hydrocarbon fluids, the gas may be passed through an absorption tower containing a scavenging formulation.

 One advantage of the use of the alpha-amino ether scavenger over other scavengers is that the alpha-amino ether scavenger is soluble in hydrocarbon fluids, since it is not
15 a water-based product.

 As illustrated in FIG. 1, in at least one embodiment the hydrogen sulfide scavenger is produced by reacting a secondary amine with formaldehyde or other formaldehyde equivalents such as paraformaldehyde or s-trioxane. This produces a composition of matter that predominantly comprises two forms of alpha-amino ethers (compounds B and C). 10%-25% of
20 the composition is a mono oxygen ether (compound B) and 50%-80% of the composition is a bis oxygen ether with a single carbon atom between the ether oxygens (compound C). The reaction product also comprises 10-25% of the non-ether diamine (compound A). Compound A is an unavoidable side product of the reaction mixture. The reaction can be performed by mixing the reactants in solvents such as but not limited to Naphtha (Petroleum) Heavy Aromatic Solvents

(such as Aromatic 150 and Solvesso by ExxonMobil) or Naphtha Light Aromatic Solvents (such as (Aromatic 100 by Americhem Sales Corporation).

In at least one embodiment the ratio of amine to formaldehyde in the reaction mixture is inclusively within the range of 1.5:1 to 1:1.5 and is preferably between 1.2:1 and 1:1.2.

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In at least one embodiment any of the R and R' groups correspond to any of the R₁, R₂, R₃, and R₄, groups described in the definition of "alpha-amino ether".

In at least one embodiment when R is n-butyl and R' is H then:

Compound A is N,N,N',N'-tetrabutylmethanediamine,

10 Compound B is N,N'-oxybis(methylene)bis(N,N-dibutylene), and

Compound C is N,N'-(methylenebis(oxy)bis(methylene))bis(N,N'-dibutylamine).

At least some contemplated scavenging compositions include formulations comprising:

(Compound A, B, and C), (A and B), (A and C), (B and C), (C alone), and (B alone).

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EXAMPLES

The foregoing may be better understood by reference to the following example, which is presented for purposes of illustration and is not intended to limit the scope of the invention.

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Samples of hydrocarbon fluids were tested to determine the efficiency of the scavenger. Table 1 compares the inventive composition in naphtha at 22 degrees C, Table 2 kerosene at 22 degrees C, and Table 3 slurry oil (such as carbon black oil, decant oil, and clarified slurry oil produced in a refinery) at 97 degrees C. The samples contained variable levels of hydrogen sulfide and were comparatively treated with various

dosages of alpha-amino ether scavenger or left untreated, and the amounts H₂S reduced in each sample was recorded.

Table 1: Naphtha 22 °C

Treatment	H ₂ S levels (ppm)	ppm H ₂ S Reduced	Percent Reduction	Dose Ratio	Time
Untreated	800				
Compounds A - C	20	780	97.5	0.2	2 h
Compounds A - C	6	794	99.2	0.3	2 h
Compounds A - C	3	797	99.6	0.2	24 h
Compounds A - C	<1	>799	99.9	0.3	24h
Compounds A - C	12 (4)	788 (796)	98.5 (99.5)	0.2	2 h (24h)

Table 2: Kerosine 22 °C

Treatment	H ₂ S levels (ppm)	ppm H ₂ S Reduced	Percent Reduction	Dose Ratio	Time
Untreated	1400				
Compounds A - C	400	1000	71	0.1	2 h
Compounds A - C	220	1180	84	0.2	2 h
Compounds A - C	95	1305	93	0.3	2 h

Table 3: Slurry oil 97 °C

Treatment	H ₂ S levels (ppm)	ppm H ₂ S Reduced	Percent Reduction	Dose Ratio	Time
Untreated	1300				
Compounds A - C	450	850	65	0.1	2.5 h
Compounds A - C	240	1060	82	0.2	2.5 h
Compounds A - C	180	1120	86	0.3	2.5 h
Compounds A - C	140	1160	89	0.4	2.5 h
Compounds A - C	90	1210	93	0.5	2.5 h

The amount of H₂S present in the vapor space was determined by measuring the vapor space hydrogen sulfide levels according to ASTM D5705-03. The test procedure was modified by running at temperatures other than 60°C. A one-gallon sample was divided into multiple 500 milliliter samples for testing. The treated containers were pre-dosed with Compounds A-C and then the fluid being tested was poured into the container.

In each example, the dose ratio was the number used to determine the ppm

treat rate for the sample. For table 1 the untreated sample resulted in a vapor space hydrogen sulfide measurement of 800 ppm. A dose ratio of 0.2 indicates the sample was treated with 160 ppm of additive. A dose ratio of 0.3 indicates that the sample was treated with 240 ppm of additive.

5 This data demonstrates that the presence of the alpha-amino ether scavenger reduced the H₂S in the hydrocarbon fluids in a relatively short amount of time and continued to reduce the H₂S the longer the sample was exposed to the alpha-amino ether prior to testing.

 While this invention may be embodied in many different forms, there are
10 shown in the drawings and described in detail herein specific preferred embodiments of the invention. The present disclosure is an exemplification of the principles of the invention and is not intended to limit the invention to the particular embodiments illustrated. All patents, patent applications, scientific papers, and any other referenced materials mentioned herein are incorporated by reference in their entirety. Furthermore,
15 the invention encompasses any possible combination of some or all of the various embodiments described herein and incorporated herein.

 The above disclosure is intended to be illustrative and not exhaustive. This description will suggest many variations and alternatives to one of ordinary skill in this art. All these alternatives and variations are intended to be included within the scope of the claims where
20 the term "comprising" means "including, but not limited to". Those familiar with the art may recognize other equivalents to the specific embodiments described herein which equivalents are also intended to be encompassed by the claims.

 All ranges and parameters disclosed herein are understood to encompass any and all subranges subsumed therein, and every number between the endpoints. For example, a stated

range of “1 to 10” should be considered to include any and all subranges between (and inclusive of) the minimum value of 1 and the maximum value of 10; that is, all subranges beginning with a minimum value of 1 or more, (e.g. 1 to 6.1), and ending with a maximum value of 10 or less, (e.g. 2.3 to 9.4, 3 to 8, 4 to 7), and finally to each number 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 contained
5 within the range.

This completes the description of the preferred and alternate embodiments of the invention. Those skilled in the art may recognize other equivalents to the specific embodiment described herein which equivalents are intended to be encompassed by the claims attached hereto.

Claims

1. A method of reducing the amount of hydrogen sulfide in a hydrocarbon fluid by contacting that fluid with an effective amount of a composition comprising a hydrogen sulfide scavenger, wherein the amount of hydrogen sulfide scavenger is sufficient to react with the
5 hydrogen sulfide to reduce the hydrogen sulfide found in the vapor phase., the reaction product of the hydrogen sulfide scavenger and the hydrogen sulfide remain soluble in the hydrocarbon fluid, the hydrogen sulfide scavenger contains at least one alpha-amino ether.
2. The method of claim 1 wherein the composition includes one item selected from the list consisting of:
10 N,N'-oxybis(methylene)bis(N,N-dibutylamine),
N,N'-(methylenebis(oxy)bis(methylene))bis(N,N-dibutylamine),
and any combination thereof that may include N,N,N',N'-tetrabutylmethanediamine.
3. The method of claim 1 in which the reaction product of the sulfide scavenging formulation and the hydrogen sulfide do not form a separate fluid layer.
- 15 4. The method of claim 1 further comprising the step of reacting a secondary amine with a formaldehyde equivalent to form at least some of the scavenging formulation.