

USE OF ALPHA-AMINO ETHERS FOR THE REMOVAL OF MERCAPTANS FROM HYDROCARBONS

Cross-Reference to Related Applications

None.

5 Statement Regarding Federally Sponsored Research or Development

Not Applicable.

Background of the Invention

The present invention relates to the scavenging of mercaptans in hydrocarbon fluids and more particularly to the use of alpha-amino ethers as mercaptan scavengers.

10 Hydrocarbon fluids, such as crude oil, crude oil emulsions, oilfield condensate, petroleum residues and refined fuels such as naphtha, kerosene, gasoline, and other purified petroleum products often contain a variety of mercaptans, including mercaptans of relatively low molecular weight. Because of the volatility of these low molecular weight mercaptans (for example, methyl mercaptan, CH_3SH , ethyl mercaptan, $\text{CH}_3\text{CH}_2\text{SH}$, and propyl mercaptan, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$), they
15 tend to evolve into vapor spaces, where their offensive odors create problems in and around storage areas and throughout pipelines and shipping systems used for transporting the hydrocarbon.

Various additives have been employed in efforts to alleviate these problems. For example, choline or choline hydroxide has been found to alleviate hydrogen sulfide evolution and
20 to scavenge mercaptans as shown in US Patents 4,594,147, 4,867,865, and 5,183,560. However, choline and choline hydroxide are not well suited for many uses and media, such as in crude oil. Although choline and choline hydroxide might scavenge mercaptans in such media, they also form a volatile and malodorous by-product with the sulfur compounds indigenous to such media. Accordingly, the use of choline and choline hydroxide to control odors associated with light

weight mercaptans is self-defeating in media such as crude oil. European Patent Application 0 538 819 A3 describes the use of oil-soluble quaternary ammonium compounds to scavenge mercaptans from certain oils, especially high boiling, heavy residual fuels. US Patent 5,840,177 describes using quaternary ammonium hydroxides to scavenge mercaptans from certain hydrocarbon fluids.

Despite these attempts however there is still a need for compositions that are produced in high yields and low cost, and that reduce mercaptan concentrations more effectively than the prior art. Thus there is clear need and utility for compositions and methods for scavenging molecular weight mercaptans more effectively and more efficiently. 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

In an aspect, there is provided a method of reducing the amount of mercaptans in a hydrocarbon fluid comprising contacting the fluid with an effective amount of alpha-amino ether sufficient to convert the mercaptan into a non-volatile species and facilitating the removal of the volatile species from the hydrocarbon liquid thereby reducing the amount of mercaptans released into the vapor phase.

At least one embodiment of the present disclosure is directed towards a method of reducing the amount of mercaptans in a hydrocarbon fluid. The method comprises contacting the fluid with an effective amount of alpha-amino ether sufficient to convert the mercaptan into a non-volatile species.

The hydrocarbon fluid can be a liquid. The hydrocarbon fluid can be selected from the list consisting of but not limited to diesel fuel, kerosene, and gasoline. . The alpha-amino ether can be selected from the list consisting of:

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

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

4,4'-oxybis(methylene)dimorpholine,
 bis(morpholinomethoxy)methane,
 1,1'-oxybis(methylene)dipiperidine,
 bis(piperidinomethoxy)methane,
 5 N,N'-oxybis(methylene)bis(N,N-dipropylamine),
 N,N'- (methylenebis(oxy)bis(methylene))bis(N,N-dipropylamine),
 1,1'-oxybis(methylene)dipyrrolidine,
 bis(pyrrolldinomethoxy)methane,
 N,N'-oxybis(methylene)bis(N,N-diethylamine),
 10 N,N'- (methylenebis(oxy)bis(methylene))bis(N,N-diethylamine),
 and any combination thereof.

The mercaptans can be present in the hydrocarbon fluid in amounts in excess of 500 ppm. The ratio of alpha-amino ether molecules to mercaptan molecules can be within the range of 1:1000 to 1000:1.

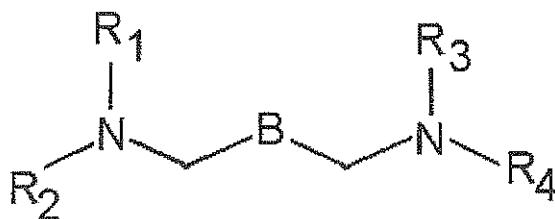
15 Description of the Drawings

FIG.1 illustrates compositions of matter useful as a mercaptan scavenger.

Detailed Description of the Invention

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

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



Where: R_1, R_2, R_3, R_4 , 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
5 an ether group, which is either an oxygen atom or a group having an oxygen atom at both ends (such as $-OCH_2O-$ or $-OC_2H_4O-$).

“Hydrocarbon fluid” means a liquid or gas predominantly comprising organic 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
10 fuel, bunker fuel oils, and any combination thereof.

“Mercaptan” means a sulfur-containing organic compound with the general formula RSH where R is any alkyl, aromatic or cyclic group. Examples of common mercaptans are methylmercaptan CH_3SH , ethylmercaptan CH_3CH_2SH , propylmercaptan $CH_3(CH_2)_2SH$, isopropylmercaptan $(CH_3)_2CHSH$, Phenylmercaptan C_6H_5SH .

15 “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 mercaptans, in a fluid medium.

“Formaldehyde equivalent” means a composition of matter containing at least one group according to the formula: $(CH_2O)_n$ in which n is an integer greater than or equal to 1, and/or a
20 composition of matter including formaldehyde or related molecules such as paraformaldehyde, and/or s-trioxane.

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.

In at least one embodiment, the amount of mercaptans in a hydrocarbon fluid is reduced by the introduction of an alpha-amino ether into the fluid. The alpha-amino ether scavenges mercaptan by forming stable non-volatile compounds. The new sulfur containing compounds are higher molecular weight and lower volatility mitigating the odor associated with volatile mercaptans.

As illustrated in FIG. 1, in at least one embodiment the mercaptan 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. 10%-25% of the composition is a single oxygen ether and 50%-80% of the composition is a double oxygen ether with a single carbon atom between the ether oxygen atoms. The reaction product also comprises 10-25% double amine that is non-reactive to the mercaptans. In FIG 1, any of the 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 the reaction is performed without solvent. This reaction can be performed with solvents such as aromatic 150, aromatic 100, etc. to create a diluted product.

In at least one embodiment a scavenging formulation is used in a hydrocarbon fluid. The formulation can but is not required to contain a solvent and at

least one alpha-amino ether, the alpha-amino ether can be used without solvent. The solvent is selected from the list consisting of water, alcohol, aromatic solvent, non-aromatic solvent and a solvent that solvates alpha-amino ethers, and any combination thereof. The formulation can be introduced into the hydrocarbon fluid by mechanical means including but not limited to injection pumps or any other mechanism known in the art including but not limited to those methods described in US Patent 5,840,177.

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.

Samples of kerosene were treated with known amounts of mercaptans and were tested according to ASTM D5623-94. In the test procedure described by ASTM D5623-94 the oven temperature increases from 10 °C (50 °F) to 250 °C (482 °F) at a rate of 10 °C/min. Any sulfur containing compound that passes through the GC column up to the endpoint and does not have a retention time calibrated to a known structure is listed as an unidentified volatile compound.

Table 1 shows the ppm wt of sulfur in the form of sec-butyl mercaptan and n-butyl mercaptan in the untreated sample. Tables 2 and 3 show the reduction in mercaptans when treated with alpha-amino ethers derived from butyl amine and morpholine respectively. The loss of n-butyl mercaptan and increase in unidentified volatile sulfur compounds indicates that the mercaptan has formed a stable compound that did not match a known standard.

Untreated Sample
Sulfur Speciation ASTM D-5623

<i>Mercaptan</i>	<i>ppm wt Sulfur</i>
sec-Butyl Mercaptan	1.5
n-Butyl Mercaptan	396

Table 1

N,N'-oxybis(methylene)bis(N,N-dibutylamine) and
N,N'-(methylenebis(oxy)bis(methylene))bis(N,N-dibutylamine)
Sulfur Speciation ASTM D-5623

<i>Mercaptan</i>	<i>ppm wt Sulfur</i>	<i>Sulfur Reduction</i>	<i>% Reduction</i>
sec-Butyl Mercaptan	<0.2	>1.3	>87
n-Butyl Mercaptan	6.8	389.2	98.3
Unidentified Volatile Sulfur	388		

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Table 2

4,4'-oxybis(methylene)dimorpholine and
bis(morpholinomethoxy)methane
Sulfur Speciation ASTM D-5623

<i>Mercaptan</i>	<i>ppm wt Sulfur</i>	<i>Sulfur Reduction</i>	<i>% Reduction</i>
sec-Butyl Mercaptan	0.4	1.1	73
n-Butyl Mercaptan	45	351	88.6
Unidentified Volatile Sulfur	343		

Table 3

10 To further illustrate the effectiveness of alpha-amino ethers as mercaptan scavengers, 9

different mercaptans were mixed together (Tables 4 and 5). The mercaptan mixture (1000 ppm v/v) was added to kerosene and then the ppm wt of the sulfur species was measured according to ASTM D5623-94. Various alpha-amino ethers (Tables 6 – 10) were used to treat the mercaptans by adding 3000 ppm v/v of various alpha-amino ethers. The decrease in the individual mercaptan components and the corresponding increase in unidentified volatile sulfur species demonstrates that the mercaptans reacted with the alpha-amino ethers to form stable compounds of lower volatility.

A complex mercaptan solution of nine different mercaptans was prepared and a series of alpha amino ethers was tested for their ability to reduce the mercaptans. 1000 ppm (v/v) was added to a solution of kerosene. The kerosene was then treated with 3000 ppm (v/v) of the specified samples.

			Untreated Sample Sulfur Speciation ASTM D-5623	
<i>Mercaptan</i>	<i>Mass %</i>	<i>Mole %</i>	<i>Mercaptan</i>	<i>ppm wt Sulfur</i>
Ethyl	11.1	15.7	Ethyl	57
Isopropyl	11.1	12.8	Isopropyl	48
tert-Butyl	11.1	10.8	tert-Butyl	45
n-Propyl	11.1	12.8	N-Propyl	49
Isobutyl	11.1	10.8	Isobutyl	42
n-Butyl	11.1	10.8	N-Butyl	43
Phenyl	11.1	8.9	Phenyl	35
Benzyl	11.1	7.9	Benzyl	33
n-Amyl	11.1	9.5	Unidentified (n-Amyl)	40

Tables 4 and 5

**N,N'-oxybis(methylene)bis(N,N-dibutylamine) and
N,N'-(methylenebis(oxy)bis(methylene))bis(N,N-dibutylamine)**
Sulfur Speciation ASTM D-5623

<i>Mercaptan</i>	<i>ppm wt Sulfur</i>	<i>Sulfur Reduction</i>	<i>% Reduction</i>
Ethyl	0.4	56.6	99.3
Isopropyl	0.4	47.6	99.2
tert-Butyl	1.0	44.0	97.8
N-Propyl	0.3	48.7	99.4
Isobutyl	0.4	41.6	99.0
N-Butyl	0.4	42.6	99.1
Phenyl	0.8	34.2	97.7
Benzyl	0.6	32.4	98.2
Unidentified	416		

Table 6

**1,1'-oxybis(methylene)dipiperidine and
bis(piperidinomethoxy)methane
Sulfur Speciation ASTM D-5623**

<i>Mercaptan</i>	<i>ppm wt Sulfur</i>	<i>Sulfur Reduction</i>	<i>% Reduction</i>
Ethyl	0.2	56.8	99.6
Isopropyl	<0.2	>47.8	>99.6
tert-Butyl	0.3	44.7	99.3
N-Propyl	0.2	48.8	99.6
Isobutyl	<0.2	>41.8	>99.6
N-Butyl	<0.2	>42.8	>99.6
Phenyl	0.3	34.7	99.1
Benzyl	0.4	32.6	98.8
Unidentified	431		

Table 7

**4,4'-oxybis(methylene)dipmorpholine and
bis(morpholinomethoxy)methane
Sulfur Speciation ASTM D-5623**

<i>Mercaptan</i>	<i>ppm wt Sulfur</i>	<i>Sulfur Reduction</i>	<i>% Reduction</i>
Ethyl	<0.2	>56.8	>99.6
Isopropyl	<0.2	>47.8	>99.6
tert-Butyl	0.2	44.8	99.6
N-Propyl	<0.2	>46.8	>99.6
Isobutyl	0.3	41.7	99.3
N-Butyl	0.2	42.8	99.5
Phenyl	0.4	34.6	98.9
Benzyl	1.5	31.5	95.5
Unidentified	437		

Table 8

**1,1'-oxybis(methylene)dipyrrolidine and
bis(pyrrolidinomethoxy)methane
Sulfur Speciation ASTM D-5623**

<i>Mercaptan</i>	<i>ppm wt Sulfur</i>	<i>Sulfur Reduction</i>	<i>% Reduction</i>
Ethyl	0.2	56.8	99.6
Isopropyl	<0.2	>47.8	>99.6
tert-Butyl	0.2	44.8	99.6
N-Propyl	0.2	48.8	99.6
Isobutyl	0.2	41.8	99.5
N-Butyl	0.2	42.8	99.5
Phenyl	0.4	34.6	98.9
Benzyl	<0.2	>32.8	>99.4
Unidentified	411		

Table 9

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**N,N'-oxybis(methylene)bis(N,N-diethylamine) and
N,N'-(methylenebis(oxy)bis(methylene))bis(N,N-diethylamine)
Sulfur Speciation ASTM D-5623**

<i>Mercaptan</i>	<i>ppm wt Sulfur</i>	<i>Sulfur Reduction</i>	<i>% Reduction</i>
Ethyl	0.2	56.8	99.6
Isopropyl	0.2	47.8	99.6
tert-Butyl	0.3	44.7	99.3
N-Propyl	0.2	48.8	99.6
Isobutyl	<0.2	>41.8	>99.5
N-Butyl	0.2	42.8	99.5
Phenyl	<0.2	>34.6	>99.4
Benzyl	<0.2	>32.8	>99.4
Unidentified	436		

Table 10

The previous data makes clear that the addition of an alpha-amino ether to a hydrocarbon fluid reduces the mercaptan to a non-volatile sulfur species and thereby scavenges

10 mercaptans from the hydrocarbon fluid.

While this invention may be embodied in many different forms, there are

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, 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 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 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 mercaptans in a hydrocarbon fluid comprising contacting the fluid with an effective amount of alpha-amino ether sufficient to convert the mercaptan into a non-volatile species and facilitating the removal of the volatile species from the hydrocarbon liquid thereby reducing the amount of mercaptans released into the vapor phase
2. The method of claim 1 wherein the hydrocarbon fluid is liquid.
3. The method of claim 1 wherein the hydrocarbon fluid is selected from the list consisting of products produced from crude oils such as but not limited to kerosene, diesel fuel, gasoline, naphtha and heavy aromatic naphtha.
4. The method of claim 1 wherein there are different kinds of mercaptans in the hydrocarbon fluid.
5. The method of claim 1 wherein the alpha-amino ether is selected from the list consisting of:
 - N,N'-oxybis(methylene)bis(N,N-dibutylamine),
 - N,N'- (methylenebis(oxy)bis(methylene))bis(N,N-dibutylamine),
 - 4,4'-oxybis(methylene)dimorpholine,
 - bis(morpholinomethoxy)methane,
 - 1,1'-oxybis(methylene)dipiperidine,
 - bis(piperidinomethoxy)methane,
 - N,N'-oxybis(methylene)bis(N,N-dipropylamine),
 - N,N'- (methylenebis(oxy)bis(methylene))bis(N,N-dipropylamine),
 - 1,1'-oxybis(methylene)dipyrrolidine,
 - bis(pyrrolldinomethoxy)methane,
 - N,N'-oxybis(methylene)bis(N,N-diethylamine),

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

and any combination thereof.

6. The method of claim 1 wherein the ratio of alpha-amino ether molecules to mercaptan molecules is within the range of 1:1000 to 1000:1.

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