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Canadian Intellectual Property Office

CA 2805402 C 2018/03/13

(11)(21) **2 805 402**

(12) BREVET CANADIEN / CANADIAN PATENT

(13) **C**

(86) **Date de dépôt PCT/PCT Filing Date:** 2011/07/13
(87) **Date publication PCT/PCT Publication Date:** 2012/01/19
(45) **Date de délivrance/Issue Date:** 2018/03/13
(85) **Entrée phase nationale/National Entry:** 2013/01/14
(86) **N° demande PCT/PCT Application No.:** US 2011/043780
(87) **N° publication PCT/PCT Publication No.:** 2012/009391
(30) **Priorité/Priority:** 2010/07/14 (US12/835,805)

(51) **Cl.Int./Int.Cl.** ***C10G 29/20*** (2006.01),
C07C 7/152 (2006.01)

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(54) **Titre : PROCEDE AMELIORE POUR EXTRAIRE DU SULFURE D'HYDROGENE**
(54) **Title: IMPROVED METHOD OF REMOVING HYDROGEN SULFIDE**

(57) **Abrégé/Abstract:**
The invention provides a method of removing hydrogen sulfide from hydrocarbon fluids. The method involves using a nitroxide molecule to promote a sulfide scavenger such as alkyl-triazine. The nitroxide effectively accelerates the scavengers activity. This allows for the avoidance of the introduction of halides into the hydrocarbon stream.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 January 2012 (19.01.2012)

PCT

(10) International Publication Number
WO 2012/009391 A3

(51) International Patent Classification:
C10G 29/20 (2006.01) *C07C 7/152* (2006.01)

(21) International Application Number:
PCT/US2011/043780

(22) International Filing Date:
13 July 2011 (13.07.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/835,805 14 July 2010 (14.07.2010) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(88) Date of publication of the international search report:
10 May 2012

WO 2012/009391 A3

(54) Title: IMPROVED METHOD OF REMOVING HYDROGEN SULFIDE

(57) Abstract: The invention provides a method of removing hydrogen sulfide from hydrocarbon fluids. The method involves using a nitroxide molecule to promote a sulfide scavenger such as alkyl-triazine. The nitroxide effectively accelerates the scavengers activity. This allows for the avoidance of the introduction of halides into the hydrocarbon stream.

IMPROVED METHOD OF REMOVING HYDROGEN SULFIDE

Cross-Reference to Related Applications

None.

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 streams is well known in the industry and considerable expense and efforts are 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 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 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 nontoxic 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 bc 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 a sewage gas using certain tri-substituted-hexahydro-s-triazines. German reference DE4027300 discloses a regenerative solvent for removing H_2S 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 thc combination of an alkyl triazine scavenger and quaternary ammonium salt, where the quaternary ammonium salt enhances the effectiveness of the alkyl-triazine..

Thus there is clear need and utility for an improved method of scavenging hydrogen sulfide from hydrocarbon fluids. 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.

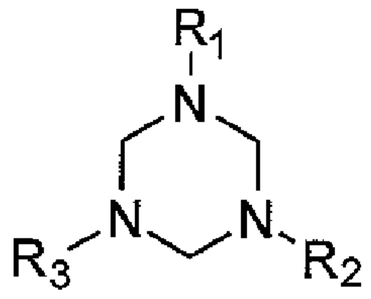
Brief Summary of the Invention

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 sulfide scavenger formulated with a nitroxide promoter. The amount of nitroxide promoter is sufficient to accelerate the scavenging action of the scavenger in comparison to the scavenging action of the scavenger in the absence of the nitroxide promoter.

Detailed Description of the Invention

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

"Alkyl-triazine" means a molecule according to the formula:

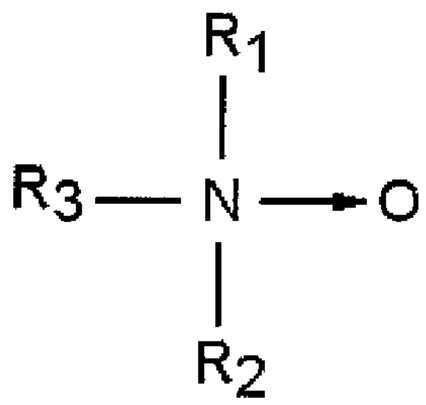


Where R_1, R_2, R_3 are Alkyl groups such as methyl, ethyl, propyl, isopropyl, t-butyl, etc. or are substituted alkyl groups such as CH_2CH_2OH, and R_1, R_2, R_3 can all be the same group or one or more different groups. Alkyl-triazines include but are not limited to the triazines disclosed in US Patent 5,744,024.

"Hydrocarbon fluid" means a liquid or gas predominantly comprising organic material including but not limited to kerosene, crude oil, distillate fuels, fuel oil, heating oils, diesel fuel, gasoline, jet fuel, bunker fuel oils, and any combination thereof.

"Methyltriazine" means an alkyl-triazine in which R_1, R_2, and R_3 are all methyl groups.

"Nitroxide" means a composition of matter according to the formula:



where R_1 R_2 and R_3 are any alkyl group containg 1 – 30 carbon atoms and includes cyclic compounds.

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

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

"Promoter" means a composition of matter that in and of itself does not scavenge, but when combined with a known scavenger, significantly increases the effectiveness of the scavenger.

"Salt" means a compound comprising an anion and a cation which usually ionizes in solution.

"Scavenger" means a composition of matter, such as but not limited to alkyl triazines, useful in reducing the amount of some other composition of matter, such as but not limited to hydrogen sulfide, in a fluid medium.

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 hydrogen sulfide in a hydrocarbon fluid is reduced by the introduction of an alkyl-triazine scavenger with a nitroxide promoter. The promoter increases the effectiveness of the alkyl-triazine scavenger. Nitroxide is superior to the prior art quarternay ammonium salt promoters because nitroxide is a single component and does not contain halides such as chloride.

The effectiveness of a nitroxide as a promoter is unexpected because it is a single neutral compound. In at least one embodiment the promoter is from 1-25% of the scavenger-promoter containing composition.

In at least one embodiment, at least a portion of the triazines are synthesized according to the process described in US Patent 5,744,024.

In at least one embodiment the ntiroxide is mixed with a solution of alkyl triazine where the solvent can be water and the nitroxide bearing solution is introduced into the hydrocarbon fluid. In at least one embodiment the nitroxide introduction is simultaneous to the alkyl-triazine introduction. The properties of the ntiroxide promoter are such that it is highly effective in a number of different hydrocarbon fluids.

One advantage of the use of the nitroxide promoter with a scavenger over the prior art scavengers is that the nitroxide promoter is not a salt (it is not a combination of an anion and a cation) and therefore lacks halides and in particular lacks chloride.

In at least one embodiment a scavenging formulation is used in a

hydrocarbon stream. The formulation comprises a solvent, alkyl-triazine, and nitroxide. The solvent is selected from the list consisting of water, alcohol, aromatic solvent, a solvent that mutually solvates alkyl-triazine, and nitroxide and any combination thereof. The formulation can be introduced into the hydrocarbon stream 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.

In at least one embodiment the hydrocarbon fluid is in a liquid state. In at least one embodiment the hydrocarbon fluid is in a gaseous state.

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 sour hydrocarbon streams (fuel oils) were tested to determine the efficiency of the triazine formulated with promoter versus the triazine formulated without a promoter. The samples were comparatively treated with various dosages of methyltriazine scavenger, methyltriazine scavenger with a promoter, and the amounts of residual H_2S for the various samples were recorded. Table 1 compares the inventive composition at different concentrations, Table 2 compares promoted scavenger with non-promoted scavenger, and table 3 compares methyltriazine with and without promoter over time.

Table 1: Comparison of promoter at 3 different concentrations in vacuum gas oil for 2 hours at 60 °C

Sample #	Treatment	Dose (ppm)	H2S (ppm)	Percent Reduction	Dose Ratio
Untreated		0	200		0
1	Methyltriazine + 2.5% nitroxide	60	100	50	0.3
2	Methyltriazine + 5% nitroxide	60	120	40	0.3
3	Methyltriazine + 10% nitroxide	60	130	35	0.3

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Table 2; Comparison of promoted and non-promoted triazine, in kerosene for 2 hours

Sample #	Treatment	Dose (ppm)	H2S (ppm)	Percent Reduction	Dose Ratio
Untreated		0	1300		
1	Methyltriazine + 5% Quaternary ammonium	260	70	95	0.2
2	Methyltriazine + 5% nitroxide	260	90	93	0.2
3	Methyltriazine	260	120	91	0.2
Untreated		0	950		
1	Methyltriazine + 5% Quaternary ammonium	284	30	97	0.3
2	Methyltriazine + 5% nitroxide	284	70	93	0.3
3	Methyltriazine	284	80	92	0.3

Table 3: Comparison of alkyl-triazine with and without promoter over time in kerosene

Sample #	Treatment	Dose (ppm)	H2S (ppm)	Percent Reduction	Dose Ratio	Time (min)
Untreated		0	1200		0	0
1	Methyltriazine + nitroxide	400	300	75	0.3	15
2	Methyltriazine + nitroxide	400	200	83	0.3	30
3	Methyltriazine + nitroxide	400	85	93	0.3	60
4	Methyltriazine + nitroxide	400	75	94	0.3	90
5	Methyltriazine + nitroxide	400	75	94	0.3	120
Untreated		0	600		0.3	0
1	Methyltriazine	200	250	58	0.3	15
2	Methyltriazine	200	230	62	0.3	30
3	Methyltriazine	200	110	82	0.3	60
4	Methyltriazine	200	60	90	0.3	90
5	Methyltriazine	200	70	88	0.3	120

The vapor space hydrogen sulfide levels were measured according to the procedure described by ASTM D5705-03. The test procedure was modified for tables 2 and 3 by performing the test in kerosene at room temperature, which was approximately 22 °C instead of 60 °C.

This data demonstrates that the presence of the nitroxide enables the methyltraizine scavenger to reduce the levels of H_2S faster than methyltriazine does without the promoter.

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. Furthermore,

the invention encompasses any possible combination of some or all of the various embodiments described herein and incorporated herein.

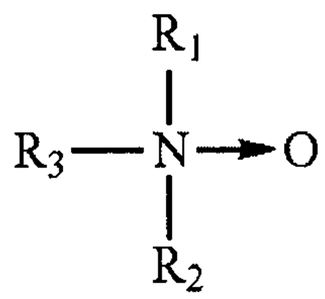
The above disclosure is intended to be illustrative and not exhaustive. This description will suggest many variations and alternatives to one of ordinary skill in this art. All these alternatives and variations are intended to be included within the scope of the claims where the term "comprising" means "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 hydrogen sulfide in a hydrocarbon fluid comprising contacting gaseous hydrocarbon fluid with an effective amount of a composition as the gaseous hydrocarbon fluid passes through an absorption tower, the composition comprising solvent, sulfide scavenger and a nitroxide promoter wherein the amount of nitroxide promoter is sufficient to accelerate the scavenging action of the scavenger in comparison to the scavenging action of the scavenger in the absence of the nitroxide promoter, wherein the scavenger is an alkyl-triazine and the solvent comprises water and wherein the nitroxide promoter is a composition of matter according to the formula:



where R_1 R_2 and R_3 are any alkyl group containing 21 – 30 carbon atoms.

2. The method of claim 1 wherein the method results in no halides being added to the hydrocarbon fluid.

3. The method of claim 1 wherein the alkyl-triazine is methyltriazine.

4. The method of claim 1 wherein the solvent also comprises at least one of: alcohol, aromatic solvent, and any combination thereof.

5. The method of claim 1 wherein R_1 R_2 and R_3 are any alkyl group containing 26 – 30 carbon atoms.