



(51) International Patent Classification:

B01J 20/22 (2006.01) **BOW 53/52** (2006.01)
C10G 29/20 (2006.01) **C02F 1/58** (2006.01)
B01D 53/14 (2006.01)

YANG, Jianzhong [CN/US]; 3602 Double Lake Drive,
 Missouri City, TX 77459 (US). **CATTANACH, Kyle, C.**
 [US/US]; 3518 Pecan Mill, Sugar Land, TX 77498 (US).

(21) International Application Number:

PCT/US201 1/0425 12

(74) **Agent: LITTLEFIELD, Stephen, A.;** Baker Hughes In-
 corporated, P.O. Box 4740, Houston, TX 77210-4740
 (US).

(22) International Filing Date:

30 June 2011 (30.06.2011)

(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.

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/360,833 1 July 2010 (01.07.2010) US
 13/172,370 29 June 2011 (29.06.2011) US

(71) **Applicant** (for all designated States except US): **BAKER
 HUGHES INCORPORATED** [US/US]; P.O. Box 4740,
 Houston, TX 77210 (US).

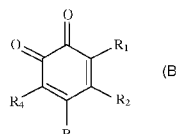
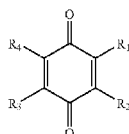
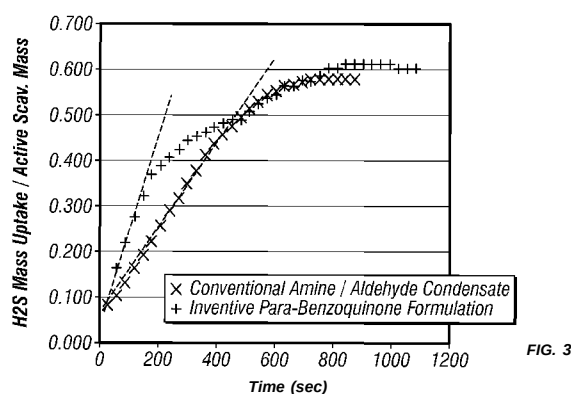
(72) Inventors; and

(75) **Inventors/Applicants** (for US only): **RAMACHAN-
 DRAN, Sunder** [US/US]; 2850 Field Line Drive, Sugar
 Land, TX 77479 (US). **JOVANCICEVIC, Vladimir**
 [US/US]; 2231 Shady Crest Drive, Richmond, TX 77469
 (US). **TSANG, Ying, H.** [US/US]; 24715 Gemstone
 Cove Court, Katy, TX 77494 (US). **SQUICCIARINI,
 Michael, P.** [US/US]; 7611 Lassiter Hollow Lane, Rich-
 mond, TX 77407 (US). **PRINCE, Philippe** [FR/US]; 915
 North Wellsford Drive, Pearland, TX 77584 (US).

(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).

[Continued on next page]

(54) **Title:** WATER-BASED FORMULATION OF H₂S/MERCAPTAN SCAVENGER FOR FLUIDS IN OILFIELD AND RE-
 FINERY APPLICATIONS



(57) **Abstract:** Hydrogen sulfide (H₂S) and/or mercaptan scavengers are chemicals that remove H₂S and/or mercaptans from gas, oil and water. Water-based formulations may be made and used employing scavenging compounds having the formulae: (A) (B) wherein each R₁, R₂, R₃, and R₄ are the same or different and are selected from the group consisting of hydrogen, an alkyl, an alkenyl, an aryl, an acyl, a halogen, a hydroxyl, a nitro, an alkyl ester, an aryl ester, an alkyl ether, an aryl ether, a hydroxymethyl, an anhydride group, an amino, and a sulfide. In one non-limiting embodiment the compounds (A) and (B) do not contain nitrogen atoms. Water-based formulations, such as those using a protic solvent with the above compounds, work well as H₂S scavengers.



Published:

- *without international search report and to be republished
upon receipt of that report (Rule 48.2(g))*

WATER-BASED FORMULATION OF H₂S/MERCAPTAN SCAVENGER FOR FLUIDS IN OILFIELD AND REFINERY APPLICATIONS

TECHNICAL FIELD

[0001] The present invention relates to methods and compositions for scavenging H₂S and/or mercaptans from fluids, and more particularly relates, in one non-limiting embodiment, to methods and compositions for scavenging H₂S and/or mercaptans from fluids having an aqueous phase, a gaseous phase and/or a hydrocarbon phase using a protic composition comprising a protic solvent and a scavenger compound.

TECHNICAL BACKGROUND

[0002] In the drilling, well completion, production, transport, storage, and processing of crude oil and natural gas, including waste water associated with crude oil and gas production, and in the storage of residual fuel oil, H₂S and mercaptans are often encountered. The presence of mercaptans is objectionable because they often react with other hydrocarbons or fuel system components. Another reason that the H₂S and mercaptans are objectionable is that they are often toxic and highly corrosive. H₂S in aqueous environments can adversely affect the integrity of pipelines, separators, storage tanks, etc. by corroding the materials of construction. Even low levels of H₂S in aqueous systems may be toxic to many living organisms. For instance, a trace amount on the order of 100 ppm may be fatal to humans. Still another reason that mercaptans are undesirable is that they have highly noxious odors. The odors resulting from mercaptans are detectable by the human nose at comparatively low concentrations and are well known. For example, mercaptans are used to odorize natural gas and used as a repellant by skunks and other animals.

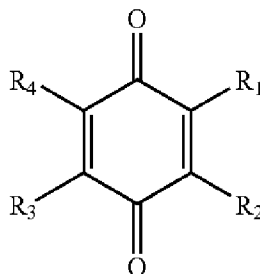
[0003] The predominant H₂S scavengers for natural gas and crude oil are monoethanolamine (MEA) and monomethylamine (MMA) triazines. These triazine compounds, which are amine/aldehyde condensates, contain nitrogen

and when used in sufficient concentration can cause problems for certain refineries. Also, the relatively high dosage rates for these triazines, and hence the higher costs, make them less desirable. In addition, there are health, safety and environmental (HS&E) concerns with H₂S scavengers that may contain formaldehyde. There have been instances where operators have required the use of a non-nitrogen containing H₂S scavenger. Glyoxal and/or acrolein have been used as a H₂S scavenger in these instances. Glyoxal is corrosive to mild steel. Acrolein is an extremely toxic substance which operators do not like to use.

[0004] Metal oxide (*e.g.* zinc oxide, ferrous oxide, etc.) solutions and caustic solutions (*e.g.* sodium hydroxide, potassium hydroxide, etc.) have also been used in the past. However, the metal oxide solutions may generate slurries and solids which have disposal issues, and the caustic solutions may be corrosive.

[0005] Hydroquinones are known to be useful as mercaptan scavengers. They are used, for example, with a basic solution to catalyze the oxidation of mercaptans to disulfides to regenerate solvent used for mercaptans exactions from crude oil. Even though hydroquinones have been widely used, their use has not been trouble free. For example, the hydroquinones require both a basic solution, such as caustic, and oxygen to be effective.

[0006] U.S. Patent Application Publication No. 2009/0095658 to Yang, et al. (Baker Hughes Incorporated) describes compounds having general formula:

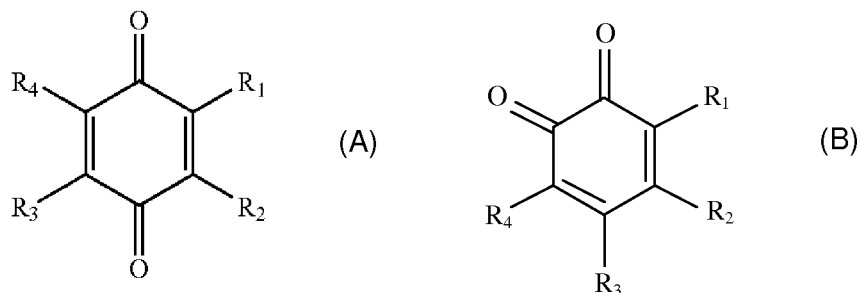


wherein each R_1 , R_2 , R_3 and R_4 are the same or different and may be hydrogen, an alkyl group, an aryl group, a halogen, a nitro group, an alkyl or aryl ester, and an alkyl or aryl ether; and other compounds where one or two of R_{1-4} are quaternary ammonium moieties. These compounds can be used as additives for crude oil and hydrocarbons. These compounds are taught as useful to scavenge mercaptans, sulfides, cyanides, and primary or secondary amines; either alone or in combination. In this Publication, these compounds have been formulated in aprotic solvents such as, but not limited to, aromatic solvents, dichloromethane, chloroform, tetrahydrofuran, N-methyl pyrrolidone, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and the like.

[0007] It would be desirable if new H_2S and/or mercaptan scavengers were discovered which could be implemented in protic solvents, and which did not necessarily contain nitrogen.

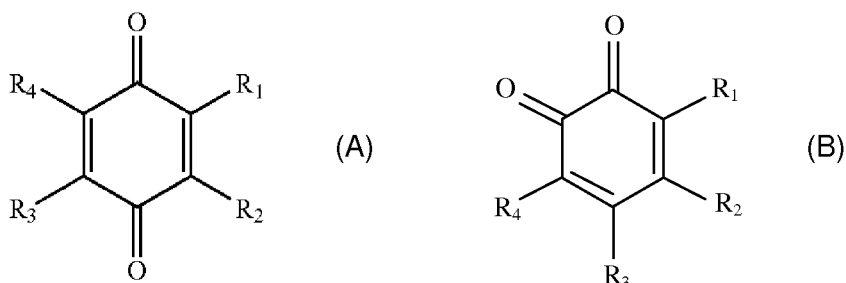
SUMMARY

[0008] There is provided in one non-limiting embodiment a method for scavenging hydrogen sulfide and/or mercaptans from a fluid. The fluid may be an aqueous phase, a gaseous phase, a mixture of an aqueous phase and a gaseous phase, a mixture of an aqueous phase and a hydrocarbon phase or a mixture of an aqueous phase, a gaseous phase and a hydrocarbon phase. The method involves contacting the fluid with an effective amount of a protic composition to reduce the amount of hydrogen sulfide and/or mercaptans as compared to an identical method absent the protic composition. The protic composition includes: a protic solvent and a compound having a formula selected from the group consisting of:



wherein each R_1 , R_2 , R_3 , and R_4 are the same or different and are selected from the group consisting of hydrogen, an alkyl, an alkenyl, an aryl, an acyl, a halogen, a hydroxyl, a nitro, an alkyl ester, an aryl ester, an alkyl ether, an aryl ether, a hydroxymethyl, an anhydride group, an amino, and a sulfide. Alternatively, none of the R groups are nitro or amino.

[0009] There is additionally provided in one non-restrictive version, a protic composition for treating fluids containing hydrogen sulfide and/or mercaptans comprising: a protic solvent and a compound having a formula selected from the group consisting of:



wherein each R_1 , R_2 , R_3 , and R_4 are the same or different and are selected from the group consisting of hydrogen, an alkyl, an alkenyl, an aryl, an acyl, a halogen, a hydroxyl, a nitro, an alkyl ester, an aryl ester, an alkyl ether, an aryl ether, a hydroxymethyl, an anhydride group, an amino, and a sulfide. In one non-limiting embodiment, none of the R groups are nitro or amino.

BRIEF DESCRIPTION OF THE DRAWINGS

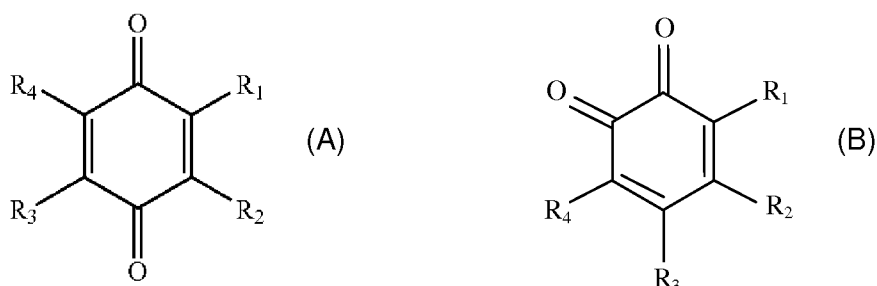
[0010] FIG. 1 is a schematic diagram of an uptake test;

[0011] FIG. 2 is a graph showing the results of a H_2S uptake test showing mass uptake as a function of time; and

[0012] FIG. 3 is a graph showing the initial rate of reaction of the ratio of H_2S mass uptake/active scavenger mass over time comparing a benzoquinone compound of a method described herein with that of a conventional amine/aldehyde condensate.

DETAILED DESCRIPTION

[0013] It has been discovered that water-based formulations of benzoquinone, specifically para-benzoquinone and ortho-benzoquinone and their derivatives are effective H_2S and/or mercaptan scavengers for many fluids, in particular for fluids having an aqueous phase, but also in other systems. The effective scavenging compounds having the general formulae:

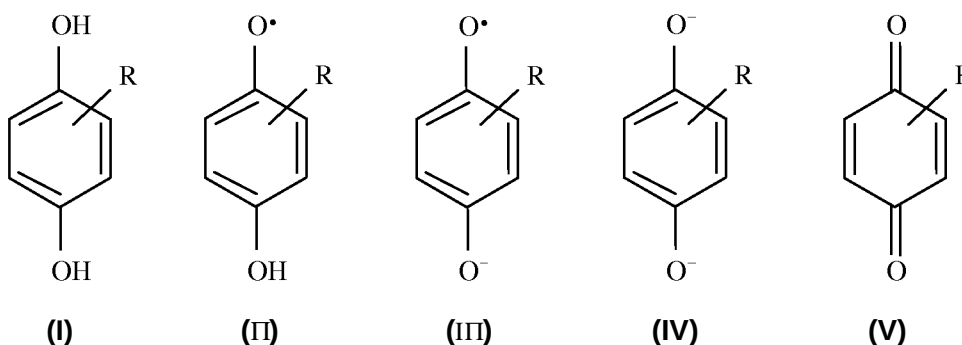


wherein each R_1 , R_2 , R_3 , and R_4 are the same or different and are selected from the group consisting of hydrogen, an alkyl, an alkenyl, an aryl, an acyl, a halogen, a hydroxyl, a nitro, an alkyl ester, an aryl ester, an alkyl ether, an aryl ether, a hydroxymethyl, an anhydride group, an amino, and a sulfide. The number of carbon atoms in the alkyl group, alkenyl group, aryl group, acyl group, alkyl ester group, aryl ester group, alkyl ether group, aryl ether, or anhydride group may range from 1 independently to 10; alternatively from 1 independently to 5. By the term "independently" as used herein with respect to ranges is meant that any lower threshold may be used together with any upper threshold to provide a valid alternative range. By a nitro group is meant $-\text{NO}_2$.

[0014] In one non-limiting embodiment, R_n is not a nitro group or an amino group to avoid the compound containing nitrogen. It has been surprisingly found that the above mentioned compounds have worked as H_2S scavengers when formulated in protic solvents such as water, methanol and ethanol, and that good results are obtained.

[0015] Aqueous solutions of both ortho- and para- quinones (formulae (B) and (A)) may be used to remove H_2S and/or mercaptans from natural gas or oil by a method involving introducing an aqueous solution of the benzoqui-

none into the gas or oil. In alkaline solutions (defined in one non-limiting embodiment as having a pH above 10), the ortho- and para- quinines, depending upon prevalent redox conditions (*i.e.* pH) may be present in fully reduced, intermediate or fully oxidized states as shown in formulae (I)-(V) below for para-quinone:



where **R** is **R₁**, **R₂**, **R₃** and/or **R₄** as previously defined. When both fully reduced (I and IV) and oxidized (V) forms of a quinine are present in alkaline solution they can exchange electrons to form semi-quinone radicals (II and III). The semi-quinone and fully oxidized quinone react with hydrogen sulfide to form an addition reaction product via an α - β conjugated system. This reaction product does not contain elemental sulfur whose presence in oil and/or gas systems is considered detrimental to the production system's integrity.

[0016] Unlike the addition reaction of H₂S with semi-quinone and fully oxidized quinine in alkaline solutions, the reaction with quinone (V) in non-aqueous solutions (defined in one non-limiting embodiment as a pH of less than 8) occurs with the formation of elemental sulfur. (For instance, see U.S. Pat. Nos. 4,592,905 and 5,180,572.)

[0017] In one non-limiting embodiment, the protic solvent may be water; alternatively the protic solvent may be alcohols, glycols and mixtures thereof alone or without water. Suitable alcohols include methanol and ethanol. Other possible solvents can be isopropyl alcohol, n-propanol and n-

butanol (n-butyl alcohol). Dimethyl formamide may also be used as an aprotic solvent.

[0018] The amount of the component (A) or (B), such as benzoquinone, in the protic composition may range from about 5 to about 40 mass %, alternatively from about 10 independently to about 30 mass %.

[0019] In one non-limiting embodiment the protic composition containing the compound has a pH of greater than 9; alternatively the composition has a pH of from about 11 to about 13.

[0020] To accomplish the rise in pH, a base may be added. Suitable bases include, but are not necessarily limited to, sodium hydroxide, potassium hydroxide and combinations thereof. The base is present in a concentration effective to give the composition a pH of greater than 9, in another non-limiting embodiment, a pH of from about 11 to about 13. There is some indication that acceptable results may be achieved with a pH of about 12.

[0021] The protic formulations or compositions may also contain a surfactant, which may act as a dispersant. Suitable surfactants that may be used include, but are not necessarily limited to, nonyl phenol ethoxylates.

[0022] It has been discovered that water-based formulations of these compounds act as hydrogen sulfide scavengers when the hydrogen sulfide is present in the aqueous phase, the gaseous phase and/or a hydrocarbon phase. The method and compositions described herein may be used to remove H₂S and/or mercaptans from aqueous systems including, but not necessarily limited hydrogen sulfide from, water injection systems, produced water from an oilfield, hydrogen sulfide present in mixed production streams and the like. These methods and compositions may also be used to remove hydrogen sulfide present in natural gas produced from natural gas wells. It is expected that the methods and compositions may be used to remove hydrogen sulfide in crude oil. These methods and compositions may also be used to remove hydrogen sulfide from brines containing hydrogen sulfide.

These methods and compositions may provide a non-nitrogen-based H₂S and/or mercaptan scavenger.

[0023] The methods described herein may involve scavenging H₂S and/or mercaptans from a fluid including an aqueous phase, a hydrocarbon phase and mixtures thereof. In this embodiment, the compound may be present in the protic or aqueous composition in a concentration from about 50 independently to about 1000 ppm; alternatively from about 50 ppm independently to about 200 ppm.

[0024] In one non-limiting embodiment the amount of the protic composition used in the fluid may range from about 50 wt% independently to about 99 wt%, alternatively from about 60 wt% independently to about 85 wt%. Alternatively, the dosage range is from about 10 independently to about 300 ppm of the active compound per ppm of the H₂S and/or the mercaptan; alternatively from about 10 independently to about 20 ppm of the active compound per ppm of the H₂S and/or the mercaptan. In one non-limiting embodiment the method is practiced in a refinery.

[0025] When the method scavenges H₂S and/or mercaptans from a gaseous phase, the method may be practiced by contacting the gaseous phase with droplets of the composition, in one non-limiting embodiment a mist, and/or passing the gaseous phase through the composition, such as through a liquid phase of the protic composition, such as by bubbling through a tower. With respect to removing H₂S and/or mercaptans from a gaseous phase, the compound is present in the protic composition in a concentration of at least 50 vol%, alternatively at least 60 vol%, alternatively at least 70 vol%, alternatively at least 80 vol%, alternatively at least 90 vol%, and alternatively at least 95 vol%.

[0026] It has also been discovered that compounds having the general formulae (A) and (B) may be effective to scavenge H₂S in gaseous systems, which formulae include benzoquinones (C₆H₄O₂) and their derivatives. Particular useful formulations include, but are not necessarily limited to 20

ppm per ppm H_2S of benzoquinone in dimethylformamide and 17 ppm benzoquinone in diglyme. However, these are aprotic solvents.

[0027] It has also been discovered that the compositions and methods herein may be used to scavenge H_2S and/or mercaptans in gaseous systems. The methods and compositions are found to have higher kinetics than conventional amine/aldehyde condensates. FIG. 3 presents a graph demonstrating that the initial rate of reaction between a compound as described herein (15 wt% para-benzoquinone, 4.5 wt% KOH and 80.5 wt% water) and H_2S is about two times faster than that of a conventional amine/aldehyde condensate. In addition, the compositions discussed herein generally provide higher H_2S -scavenging capacities than traditional amine/aldehyde condensate.

[0028] Because of this fast reaction rate, the methods and compositions described herein have an advantage to scavenge H_2S and/or mercaptans where contact time is limited. In one non-restrictive example, on offshore platforms where space is limited, and hence there are short contact times between scavengers and H_2S , often operators have to over-inject chemicals in order to reduce H_2S levels to acceptable values. However, with the methods and compositions described herein, it is expected that much shorter contact times will be needed to reduce H_2S to acceptable levels. As a result, operators do not have to build and use extra long flow loops in order to provide the extra distance (and extra contact time) that is necessary to scavenge H_2S before sales points.

[0029] Further details about the compounds and their methods of use may be found with reference to U.S. Patent Application Publication No. 2009/0095658.

[0030] The invention will now be illustrated with respect to certain examples which are not intended to limit the invention in any way but simply to further illustrate it in certain specific embodiments.

EXAMPLE 1

[0031] A formulation that contains 15 % para-benzoquinone, 4.5 % potassium hydroxide, and 80.5 % water was made. These amounts are mass %. Uptake tests were conducted with this formulation. A schematic diagram of the uptake test is shown in FIG. 1. This test was also used to generate the data of FIG. 3. The pH of this formulation was about 10.

[0032] The liquid used in the tests was Aromatic 100. Aromatic 100 is a commonly used liquid solvent identified with CAS 64742-95-6. In the tests conducted using the protic solvent based formulation, 5.05 gms of the formulation were put into 44.96 gm of Aromatic 100. The results are shown in FIG 2.

[0033] It can be seen that tests with just Aromatic 100 resulted in a mass uptake of only about 0.25 gm whereas the tests with the formulation in Aromatic 100 resulted in a mass gain of about 0.96 gm with the formulation in aromatic 100 when it was not stirred and a mass gain of about 1.14 g for the formulation in aromatic 100 that was stirred. The formulation did contain 0.228 gms of potassium hydroxide. In order to form potassium sulfide, this would react with 0.07 gms of hydrogen sulfide. Here mass gains of 0.64 gm of hydrogen sulfide were obtained for the unstirred case and 0.82 gm of hydrogen sulfide was obtained for the stirred case which can only be the result of the protic solvent based formulation.

[0034] In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been demonstrated as effective in providing methods and compositions for scavenging H₂S and/or mercaptans from aqueous fluids, hydrocarbon fluids, gaseous phases and combinations thereof. However, it will be evident that various modifications and changes can be made thereto without departing from the broader scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, specific protic solvents and hydroquinone

compounds and derivatives thereof falling within the claimed parameters, but not specifically identified or tried in a particular composition or method, are expected to be within the scope of this invention.

[0035] The words "comprising" and "comprises" as used throughout the claims is interpreted "including but not limited to".

[0036] The present invention may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed. For instance, the protic composition may consist of or consist essentially of the protic solvent and the compound of formulae (A) and (B) as the solvent and compound are defined in the claims. In another non-limiting instance, the method for scavenging hydrogen sulfide and/or mercaptans from a fluid including, but not necessarily limited to, an aqueous phase, a gaseous phase, a mixture of an aqueous phase and a gaseous phase, a mixture of an aqueous phase and a hydrocarbon phase and a mixture of an aqueous phase, a gaseous phase and a hydrocarbon phase may consist of or consist essentially of contacting the fluid with an effective amount of a protic composition to reduce the amount of hydrogen sulfide and/or mercaptans as compared to an identical method absent the protic composition, where the protic composition consists of or consists essentially of a protic solvent and a compound having a formula (A) and/or (B) as described in the claims.

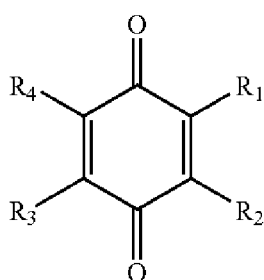
CLAIMS

What is claimed is:

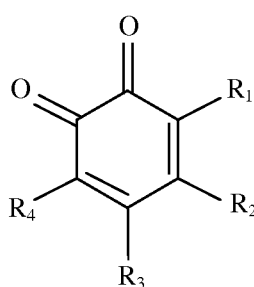
1. A method for scavenging hydrogen sulfide and/or mercaptans from a fluid comprising: contacting the fluid with an effective amount of a protic composition to reduce the amount of hydrogen sulfide and/or mercaptans as compared to an identical method absent the protic composition, the protic composition comprising:

a protic solvent; and

a compound having a formula selected from the group consisting of:



(A)



(B)

wherein each R_1 , R_2 , R_3 , and R_4 are the same or different and are selected from the group consisting of hydrogen, an alkyl, an alkenyl, an aryl, an acyl, a halogen, a hydroxyl, a nitro, an alkyl ester, an aryl ester, an alkyl ether, an aryl ether, a hydroxymethyl, an anhydride, an amino, and a sulfide, and where the fluid is selected from the group consisting of:

an aqueous phase,

a gaseous phase,

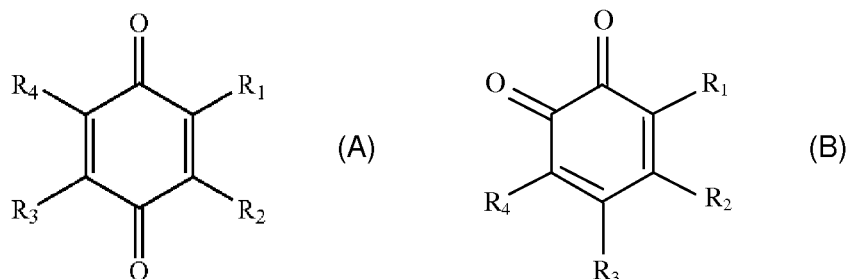
a mixture of an aqueous phase and a gaseous phase,

a mixture of an aqueous phase and a hydrocarbon phase, and

a mixture of an aqueous phase, a gaseous phase and a hydrocarbon phase.

2. The method of claim 1 where the protic composition has a pH of greater than 9.

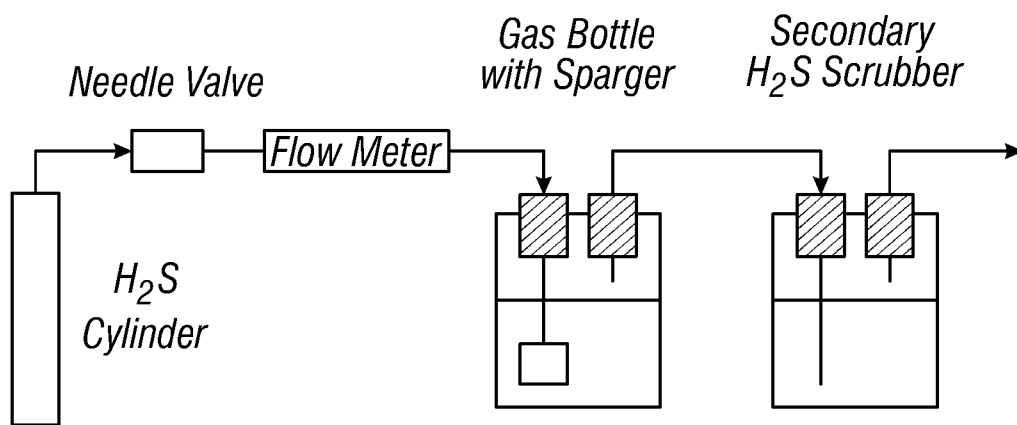
3. The method of claim 1 where the protic composition has a pH of from 11 to 13.
4. The method of claim 1 where the composition comprises a base selected from the group consisting of sodium hydroxide, potassium hydroxide and combinations thereof, the base being present at a concentration effective to give the composition a pH of greater than 9.
5. The method of claim 1, 2, 3, and 4 where the method scavenges H₂S and/or mercaptans from a fluid selected from the group consisting of an aqueous phase and mixtures of an aqueous phase and a hydrocarbon phase and the compound is present in the protic composition at a concentration of from 50 to 1000 ppm.
6. The method of claim 5 where the method is practiced in a refinery.
7. The method of claim 1, 2 or 3 where the method scavenges H₂S and/or mercaptans from a gaseous phase and the method is practiced by a process selected from the group consisting of:
 - contacting the gaseous phase with droplets of the protic composition;
 - and
 - passing the gaseous phase through the protic composition,where the compound is present in the protic composition in a concentration of at least 50 vol%.
8. A protic composition for treating fluids containing hydrogen sulfide and/or mercaptans comprising:
 - a protic solvent; and
 - a compound having a formula selected from the group consisting of:



wherein each R₁, R₂, R₃, and R₄ are the same or different and are selected from the group consisting of hydrogen, an alkyl, an alkenyl, an aryl, an acyl, a halogen, a hydroxyl, a nitro, an alkyl ester, an aryl ester, an alkyl ether, an aryl ether, a hydroxymethyl, an anhydride, an amino, a sulfide, and a hydroxide salt.

9. The protic composition of claim 8 having a pH of greater than 9.
10. The protic composition of claim 8 having a pH of from 11 to 13.
11. The protic composition of claim 8 comprising a base selected from the group consisting of sodium hydroxide, potassium hydroxide and combinations thereof, the base being present at a concentration effective to give the composition a pH of greater than 9.
12. The protic composition of claim 8, 9, 10 or 11 where the protic solvent is selected from the group consisting of water, alcohols, glycols, and combinations thereof.
13. The protic composition of claim 12 where the compound is present in the protic composition at a concentration of from 50 to 1000 ppm.
14. The protic composition of claim 12 where in the compound none of R₁, R₂, R₃, and R₄ are a nitro group or an amino group.

1/2

**FIG. 1**

2/2

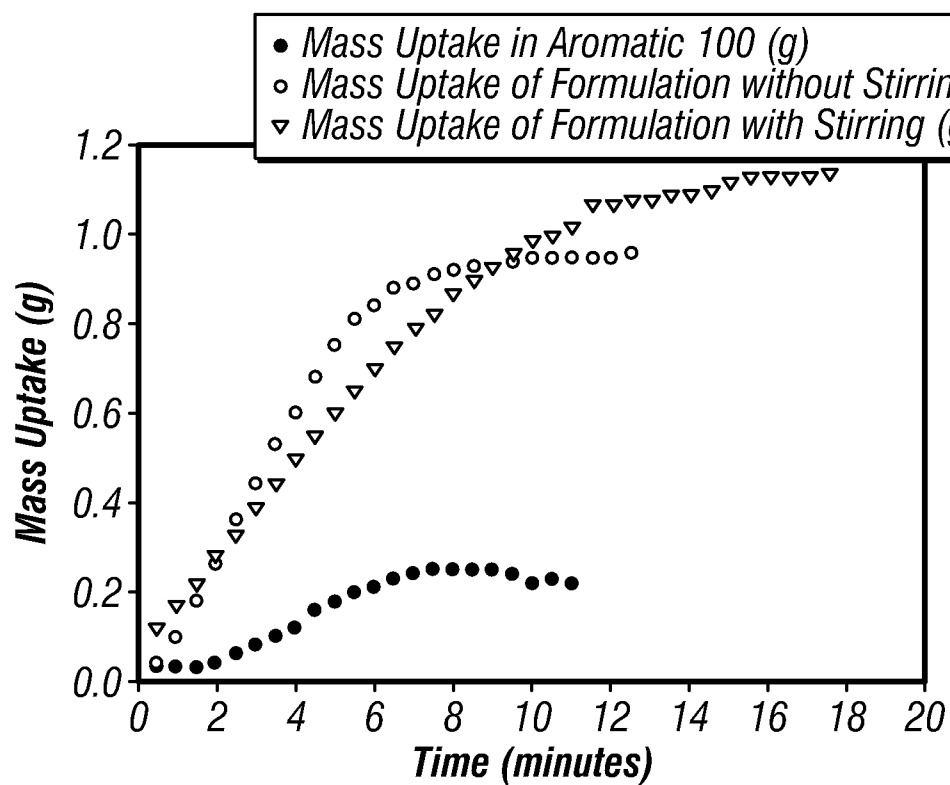


FIG. 2

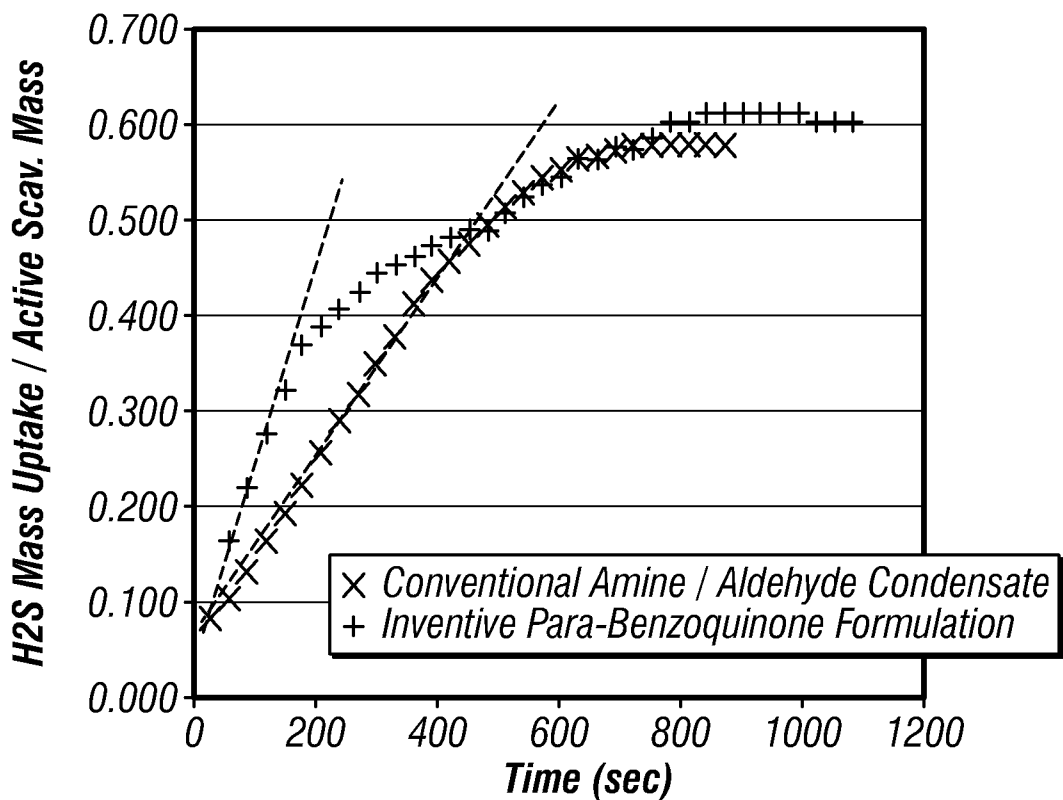


FIG. 3