

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
23 April 2009 (23.04.2009)

PCT

(10) International Publication Number
WO 2009/052127 A1(51) International Patent Classification:
C10G 29/20 (2006.01)(21) International Application Number:
PCT/US2008/079907

(22) International Filing Date: 15 October 2008 (15.10.2008)

(25) Filing Language: English

(26) Publication Language: English

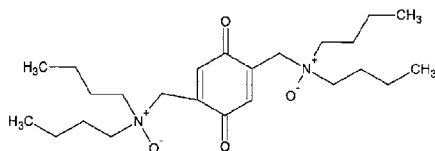
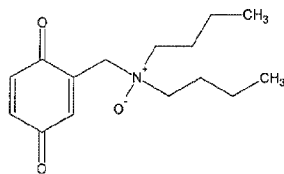
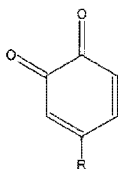
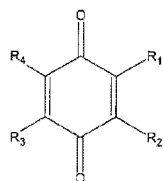
(30) Priority Data:
60/980,050 15 October 2007 (15.10.2007) US
12/250,679 14 October 2008 (14.10.2008) US(71) Applicant (for all designated States except US): **BAKER HUGHES INCORPORATED** [US/US]; 2929 Allen Parkway, Suite 2100, Houston, TX 77019-2118 (US).(72) Inventors (for US only): **YANG, Jianzhong**; 3602 Double Lake Drive, Missouri City, TX 77459 (US). **SALMA, Tauseef**; 807 Fairpark Lane, Sugar Lane, TX 77479 (US). **SCHIELD, John A.**; 9715 Harrison Lane, Missouri City, Texas 77459 (US). **WEERS, Jerry J.**; 3106 Saddle RidgeCourt, Richmond, Texas 77469 (US). **STARK, Joseph L.**; 3538 Timothy Lane, Richmond, Texas 77469 (US).(74) Agents: **LITTLEFIELD, Stephen A.** et al.; Baker Hughes Incorporated, 12645 West Airport Blvd., Sugar Land, TX 77478 (US).

(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, 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, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: MULTIFUNCTIONAL SCAVENGER FOR HYDROCARBON FLUIDS

(57) Abstract: Compounds having the formulae and general formulae 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; compounds having the general formula wherein R is an alkyl, aryl or electron withdrawing group and mixtures thereof; can be used as additives for crude oil and hydrocarbons. These compounds may be used to scavenge mercaptans, sulfides, cyanides, and primary or secondary amines; either alone or in combination.



European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, 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))*

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

MULTIFUNCTIONAL SCAVENGER FOR HYDROCARBON FLUIDS

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to scavengers. The present invention particularly relates to scavengers useful for treating crude oil and hydrocarbons.

2. Background of the Art

[0002] In the drilling, completions, 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, 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 mercaptans are objectionable is that they are often highly corrosive. 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.

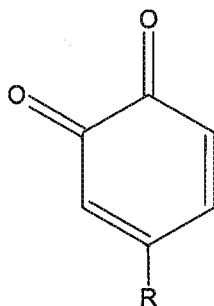
[0003] Hydroquinones are known to be useful as mercaptans scavengers. They are used, for example, with a basic solution to catalyze the oxidation of mercaptans to disulfides to regenerate solvents used for mercaptans exactions from crude oil. Even though hydroquinones have been widely used, their use has not been trouble free. For example, the hydroquinones require both a basic solution, such as caustic, and oxygen to be effective.

[0004] It would be desirable in the art to scavenge mercaptans using a composition that requires neither oxygen nor a strong base to be effective.

Summary of the Invention

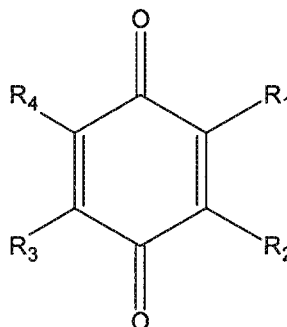
[0005] In one aspect, the invention is an additive useful for treating crude oil and hydrocarbons comprising benzoquinone.

[0006] In another aspect, the invention is an additive useful for treating crude oil and hydrocarbons comprising a compound having the general formula:



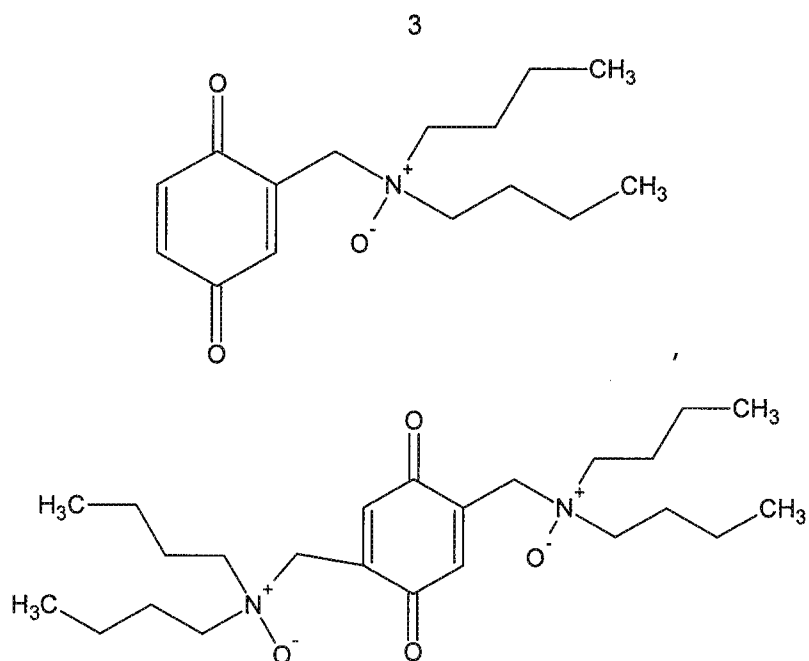
wherein R is an alkyl, aryl, or electron withdrawing group.

[0007] In another aspect, the invention is an additive useful for treating crude oil and hydrocarbons comprising compounds having the general formula:



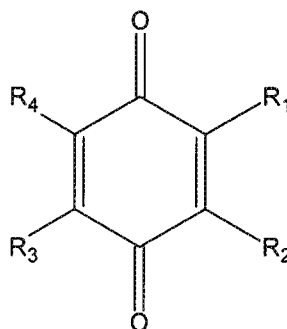
wherein each R₁, R₂, R₃ and R₄ are the same or different and may be hydrogen, an alkyl group, an aryl group, a halogen, a nitro group, an alkyl or aryl ester, and an alkyl or aryl ether.

[0008] In still another aspect, the invention is a an additive useful for treating crude oil and hydrocarbons comprising at least one compound select from the group consisting of :



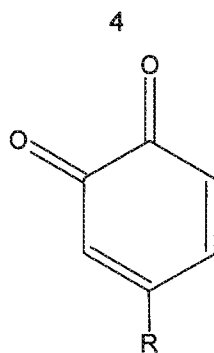
and mixtures thereof.

[0009] In still another embodiment, the invention is a method for treating a crude oil or a hydrocarbon comprising admixing crude oil or a hydrocarbon with an additive having at least one compound selected from the group consisting of compounds having the general formula:

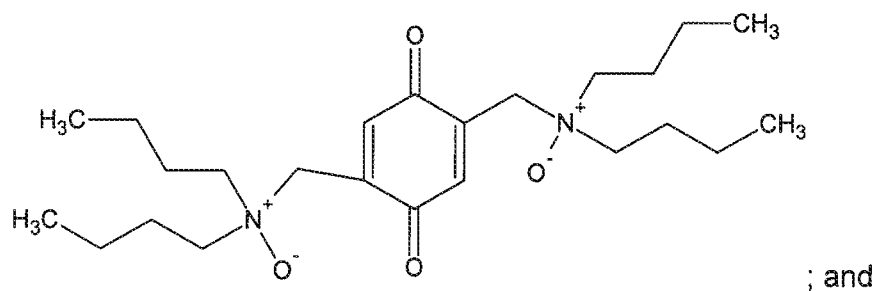
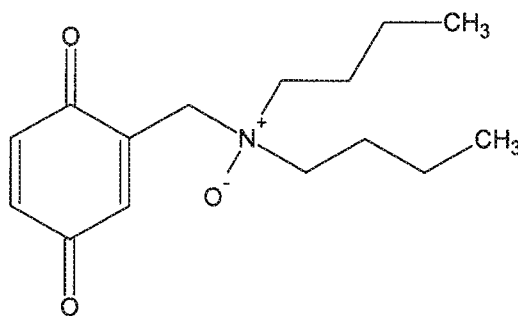


wherein each R_1 , R_2 , R_3 and R_4 are the same or different and may be hydrogen, an alkyl group, an aryl group, a halogen, a nitro group, an alkyl or aryl ester, and an alkyl or aryl ether;

compounds having the general formula:



wherein R is an alkyl or aryl group;



mixtures thereof.

Description of the Preferred Embodiments

[0010] In one embodiment, the present invention is an additive useful for treating crude oil and hydrocarbons. For the purposes of the present invention, crude oil is the fluid produced from an oil and gas well after most of the water and gases have been separated. The crude oil and hydrocarbons which may be treated using the method of the invention may have from undetectable levels of water to as much as 95 percent water. Often crude oil

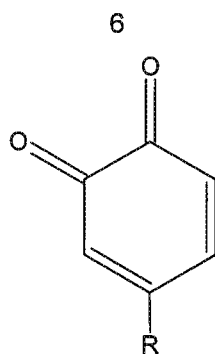
will have as much as about 15 weight percent water. In one embodiment, the crude oil and hydrocarbons may have from about 1 percent to about 10 percent water.

[0011] The hydrocarbons which may be treated using the method of the invention include any that are substantially hydrophobic. For example, fuel oils may be treated with the method of the invention. Organic chemicals and intermediates may also be treated with the method of the invention.

[0012] The additives of the invention may be used to "scavenge" mercaptans. The term "scavenge" means to either remove or change a compound such that it is less undesirable. For example, in the prior art, mercaptans were described as being scavenged by being oxidized to disulfides. The disulfides were less corrosive than the mercaptans from which they were derived and thus less undesirable.

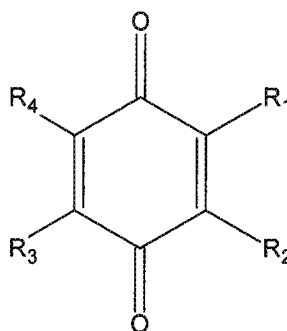
[0013] In addition to mercaptans, other classes of compounds that may be undesirable in either crude oil or hydrocarbons may be "scavenged" using the method of the invention. For example, sulfides and cyanides may be scavenged using the method of the invention. Sulfides and cyanides may be undesirable because they can render corrosion issues in downstream units even at very low ppm level. Also, they can generate highly toxic species that pose an acute health hazard. Primary and secondary amines, which may cause serious overhead corrosion and quality issue to petrochemical products, may also be scavenged using the method of the invention.

[0014] The additives useful with the method of the invention, may, in one embodiment, be prepared using benzoquinone. In another embodiment, the method of the invention may be practiced with additives including a compound having the general formula:



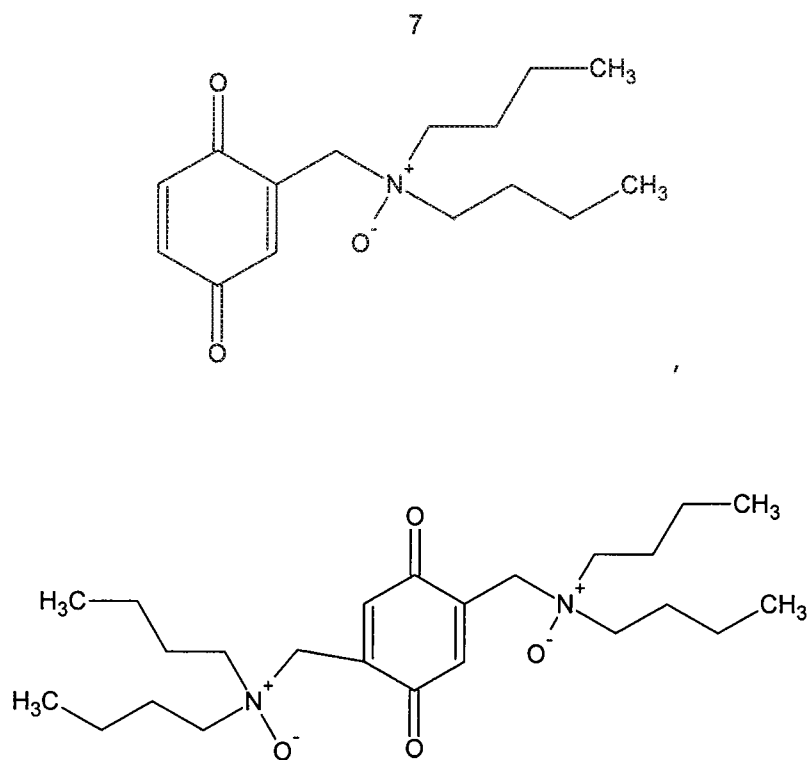
wherein R is an alkyl or aryl group. Exemplary compounds include those where the R group is hydrogen, butyl, octyl, nonyl, or with electron withdrawing groups. For example, in one embodiment of the invention, the R group is an alkyl group having from 1 to 20 carbons. In another embodiment, the R group is an alkyl group having from 4 to 12 carbons. For the purposes of this application, an electron withdrawing group is one that has a deactivating effect upon electrophilic aromatic substitution and is selected from the group consisting of $-\text{C}(=\text{O})\text{R}$, $-\text{COOR}$, $-\text{N}^+\text{R}_3$, $-\text{CN}$, $-\text{NO}_2$ etc (where R = H or alkyl or aryl group).

[0015] In still another embodiment, the method of the invention may be practiced using additives including compounds having the general formula:



wherein each R₁, R₂, R₃ and R₄ 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. For example, in one embodiment, R₂, R₃ and R₄ are hydrogen and R₁ is an alkyl group having from 1 to 12 carbons.

[0016] In another embodiment, the method of the invention may be practiced with additives including:



and mixtures thereof.

[0017] The additives of the present invention may be used in any way known to be useful to those of ordinary skill in the art of treating crude oil and hydrocarbons. For example, the additives may be used in the presence of a strong base such as sodium hydroxide and molecular oxygen. In another example of an embodiment of the invention, the additives may be used in the absence of one or both of sodium hydroxide and molecular oxygen.

[0018] Similarly, the additives may be admixed in any way known to be useful. For example, they may be added to a feed line or directly into a vessel. In one embodiment, the feed line may include a static or powered mixer. In another embodiment, the additive may be admixed by atomization into a vapor stream. In another embodiment, the vessel may include mixer or a recycle that effects mixing. In still another embodiment, the additives may be added to a pipeline and admixed by turbulence. Similarly, the additives may be added to a tank truck and mixed by the movement of the crude oil or hydrocarbon being treated with the truck.

[0019] The additives of the invention may be added in near stoichiometric amounts when the concentration of targeted contaminants and interfering compounds are known. When such concentrations are not known, then the correct dosage may be determined using jar tests or any other method well known to those of ordinary skill in the art of producing and refining crude oil and producing hydrocarbons. The additives may be used at temperatures ranging from about 0 to about 800°F.

[0020] The additives may include other compounds in addition to the components already disclosed. For example, the scavengers may also include: aromatic solvents, base, or organic oxidizers. The additives may also be prepared with any aprotic solvent such as, but not limited to dichloromethane, chloroform, tetrahydrofuran, N-methyl pyrrolidone, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), diglyme and the like.

EXAMPLES

[0021] The following examples are provided to illustrate the invention. The examples are not intended to limit the scope of the invention and they should not be so interpreted. Amounts are in volume parts or volume percentages unless otherwise indicated.

Example 1

[0022] A sample of toluene and hexane having a known amount mercaptans recorded below in Table 1 as ppm methyl mercaptans is treated with an additive of the invention wherein the additive is prepared with 20 weight percent benzoquinone in DMF. The sample is dosed with the benzoquinone solution and then shaken at 50°C for the time indicated and is then tested according to ASTM-D3227. The results are shown below in Table 1.

Example 2

[0023] Example 1 is repeated substantially identically except that naphtha is used instead of toluene and hexane mixture. The conditions and results are shown below in Table 2.

Example 3

[0024] Example 1 is repeated substantially identically except that crude oil is used instead of toluene and hexane mixture. The conditions and results are shown below in Table 3.

Table 1

Toluene

Scavenger Dose (volume ppm Benzoquinone solution)	PPM C ₄ SH	Treatment Time (hours)
0	131	--
500	122	1
1000	62	1
2000	0	1
3000	0	1

Table 2

Naphtha

Scavenger Dose (weight ppm Benzoquinone solution)	PPM SH	Treatment Time (hours)
0	907	--
4000	551	1
4000	453	24

Table 3
Crude Oil

Scavenger Dose (volume ppm Benzoquinone solution)	PPM SH	Treatment Time (hours)
0	364	24
500	351	24
1000	297	24
2000	219	24
3000	169	24

Brief Discussion of the Examples

[0025] The Examples illustrate that benzoquinone is effective at scavenging mercaptans.

Example 4

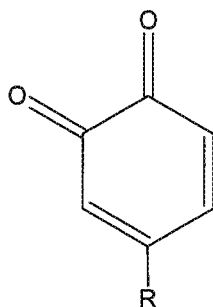
[0026] A stock solution of 1000 ppm benzylamine was prepared in aromatic solvent. The amine stock solution was then treated at room temperature with 20 weight percent benzoquinone in DMF. The amine content was analyzed with FID-GC. The results are shown below in Table 4.

Table 4

Scavenger Dose (ppm Benzoquinone)	PPM Benzylamine
0	990
200	920
400	900
800	695
1200	0

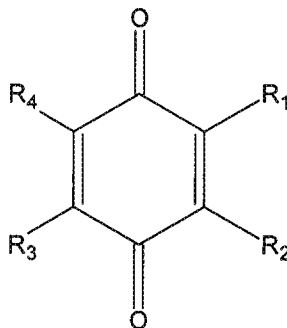
WHAT IS CLAIMED IS:

1. An additive for treating crude oil and hydrocarbons comprising a compound having the general formula:



wherein R is an alkyl, aryl or electron withdrawing group.

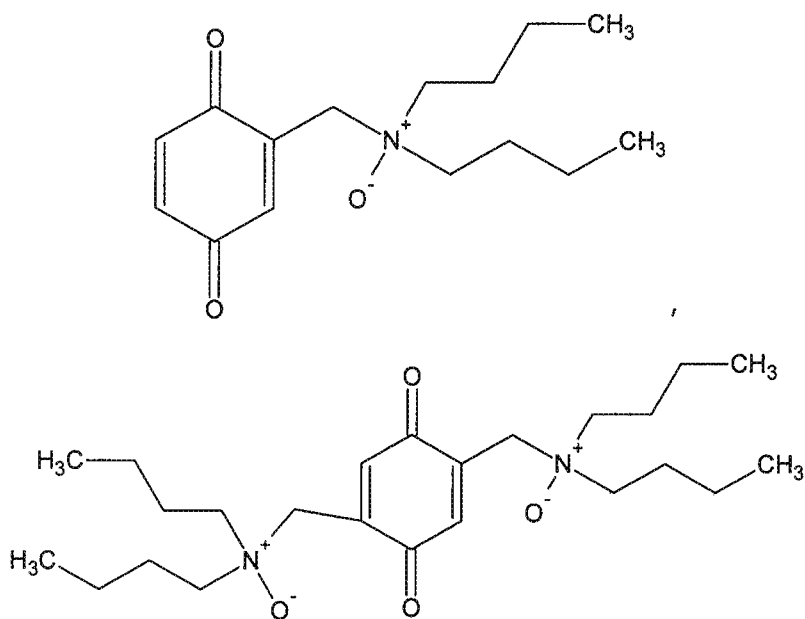
2. The additive of Claim 1 wherein R is selected from the group consisting of hydrogen, butyl, octyl, and nonyl groups.
3. The additive of Claim 1 wherein R is an alkyl group having from 1 to 20 carbons.
4. The additive of Claim 3 wherein R is an alkyl group having from 4 to 12 carbons.
5. An additive for treating crude oil and hydrocarbons comprising compounds having the general formula:



wherein each R₁, R₂, R₃ and R₄ are the same or different and are selected from the group consisting of hydrogen, an alkyl group, an aryl group, a halogen, a nitro group, an alkyl ester, an aryl ester, an alkyl ether and aryl ether.

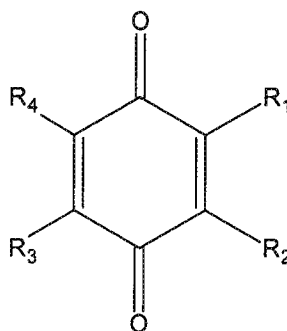
12

6. The additive of Claim 5 wherein R_1 , R_2 , R_3 and R_4 are each hydrogen.
7. The additive of Claim 5 R_1 is an alkyl group having from 1 to 12 carbons and R_2 , R_3 and R_4 are each hydrogen.
8. An additive for treating crude oil and hydrocarbons comprising at least one compound select from the group consisting of :



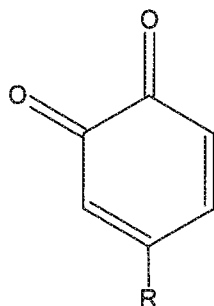
and mixtures thereof.

9. A method for treating a crude oil or a hydrocarbon comprising admixing crude oil or a hydrocarbon with an additive comprising at least one compound selected from the group consisting of:
compounds having the general formula:

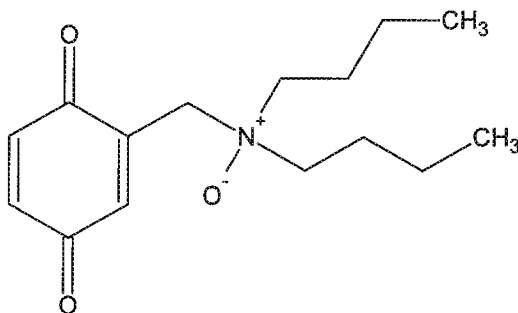


13

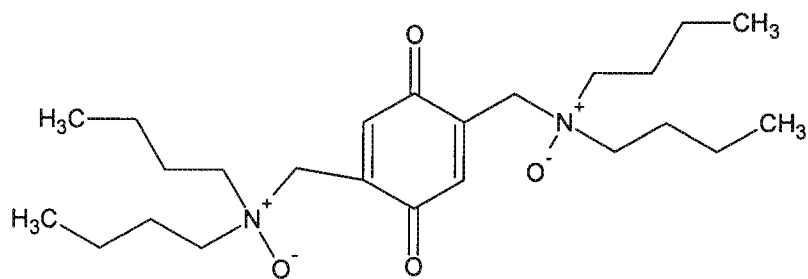
wherein each R_1 , R_2 , R_3 and R_4 are the same or different and selected from the group consisting of hydrogen, an alkyl group, an aryl group, a halogen, a nitro group, an alkyl ester, an aryl ester, an alkyl ether, and an aryl ether; compounds having the general formula:



wherein R is an alkyl or aryl group;



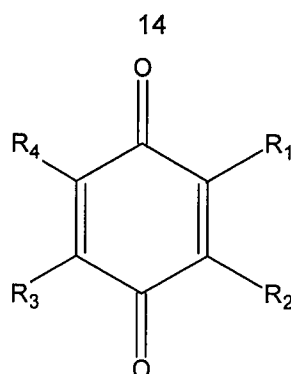
;



; and

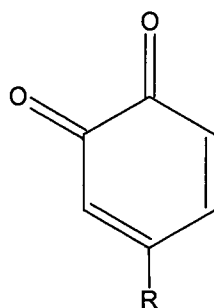
mixtures thereof.

10. The method of Claim 9 wherein the additive has the general formula:



and R_1 , R_2 , R_3 and R_4 are each hydrogen.

11. The method of Claim 9 wherein the additive has the general formula:



and R is an alkyl, aryl, or electron withdrawing group.

12. The method of Claim 11 wherein R is selected from the group consisting of hydrogen, butyl, octyl, and nonyl groups.

13. The method of Claim 9 wherein the additive is admixed with crude oil or a hydrocarbon in the presence of a strong base.

14. The method of Claim 13 wherein the strong base is molecular oxygen or sodium hydroxide.

15. The method of Claim 9 wherein the method is practiced in the absence of a strong base.

16. The method of Claim 9 wherein the method is practiced in the presence of water.

17. The method of Claim 9 wherein the water is present at a total concentration for from about 1 to about 15 percent by weight.

18. The method of Claim 9 wherein the hydrocarbon is a fuel oil.

19. The method of Claim 9 wherein the hydrocarbon is an organic chemical.
20. The method of Claim 9 wherein the additive functions to scavenge mercaptans, sulfide, cyanides, primary amines and secondary amines.
21. The method of Claim 20 wherein the additive functions to scavenge mercaptans.

A. CLASSIFICATION OF SUBJECT MATTER*C10G 29/20(2006.01)i*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC C01G 29/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS (KIPO internal) "hydrocarbon &hydrocracking &additive & benzoquinone and similar tems "

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,223,127 A(WEERS et al.)29.JUN.1993 See the whole document	1-21
A	US 5,698,696 A(MARCINIAK et al.)16.DEC.1997 See abstract, EXAMPLES	1-21
A	US 4,927,519 A(FORESTER)22.MAY.1990 See abstract, EXAMPLES	1-21



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

30 MARCH 2009 (30.03.2009)

Date of mailing of the international search report

31 MARCH 2009 (31.03.2009)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
Government Complex-Daejeon, 139 Seonsa-ro, Seo-
gu, Daejeon 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

JO Soo Ik

Telephone No. 82-42-481-5893



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2008/079907

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5223127 A	29.06.1993	CA 2071340 A1	19.01.1993
		EP 0524723 A1	27.01.1993
		JP 05-230470	07.09.1993
		JP 5230470 A	07.09.1993
		MX 9204217 A1	31.05.1994
		NO 179856 B	23.09.1996
		NO 179856 C	02.01.1997
		NO 922845 D0	17.07.1992
		NO 922845 A	19.01.1993
		OA 10063 A	14.10.1996
		US 5223127 A	29.06.1993
		WO 93-02155 A1	04.02.1993
US 5698696 A	16.12.1997	AR 001150 A1	24.09.1997
		AU 4920996 A	02.10.1996
		AU 695575 B2	13.08.1998
		CA 2215105 A1	19.09.1996
		CN 1177962	01.04.1998
		FI 973644 A	09.09.1997
		HU 9900377 A2	28.05.1999
		HU 9900377 A3	28.03.2000
		IL 117406 D0	23.07.1996
		KR 10-1998-0702883	05.08.1998
		NO 974155 A	07.11.1997
		NO 974155 D0	09.09.1997
		NZ 303012 A	29.04.1999
		NZ 332750 A	28.01.2000
		US 5698696 A	16.12.1997
		WO 96-28437 A1	19.09.1996
		ZA 9601748 A	10.09.1996
US 4927519 A	22.05.1990	CA 1329163 C	03.05.1994
		US 4828674 A	09.05.1989
		US 4927519 A	22.05.1990