HYDROGEN SULFIDE SCAVENGERS AND METHODS FOR REMOVING HYDROGEN SULFIDE FROM ASPHALT

Inventors: Sheriff ELDIN, Bellaire, TX (US); Lawrence John KARAS, Spring, TX (US)

Correspondence Address:
General Electric Company
GE Global Patent Operation
PO Box 861, 2 Corporate Drive, Suite 648
Shelton, CT 06484 (US)

Filed: Mar. 28, 2008

Publication Classification

Int. Cl.
C10G 29/20 (2006.01)

U.S. Cl. ................................................... 208/236

ABSTRACT

A method for reducing hydrogen sulfide in asphalt includes adding a hydrogen scavenger composition to the asphalt. The hydrogen sulfide scavenger includes a polyaliphatic amine having the formula 1:

\[ \text{H}_2\text{NRNH}_{(R\text{NH})_n-\text{H}} \]

R is an aliphatic radical and n is from about 0 to about 15. A method for treating asphalt and a hydrogen sulfide scavenger are also provided.
Figure 1

[Graph showing the concentration of H2S in ppm over time for samples 1 and 2.]

Figure 2

[Graph showing the concentration of H2S in ppm over time for control samples A and B.]
HYDROGEN SULFIDE SCAVENGERS AND METHODS FOR REMOVING HYDROGEN SULFIDE FROM ASPHALT

FIELD OF THE INVENTION

This invention relates generally to hydrogen sulfide scavengers and more particularly, to hydrogen sulfide scavengers for asphalt.

BACKGROUND OF THE INVENTION

During the refining of crude oil, asphalt products or heavy oil are produced as the residue from crude oil distillation. Asphalt products are black, viscous materials, which can be upgraded to higher-valued gasoline or diesel by further refining. However, asphalt products often contain hydrogen sulfide and upgrading the asphalt products increases the risk of hydrogen sulfide exposure. Since hydrogen sulfide is corrosive in the presence of water and poisonous in very small concentrations, it must be removed before the asphalt products can be upgraded.

Asphalt has a large temperature range and current commercial technology employs the use of water-based triazines as hydrogen sulfide scavengers. However, these water-based triazine materials can cause foaming, splitting and possible spillovers. Commercially available organic based scavengers are expensive and can contain metal ions. The introduction of additional metal ions can create incompatibility with up-grader catalyst beds.

What is needed is an improved organic based scavenger for removing hydrogen sulfide from asphalt.

BRIEF DESCRIPTION OF THE INVENTION

In one embodiment, a method for reducing hydrogen sulfide in asphalt, comprises adding a hydrogen sulfide scavenger composition to the asphalt, wherein the hydrogen sulfide scavenger composition comprises a polyaliphatic amine having the formula I:

\[ \text{H}_2\text{NRNH}-(\text{R}_n\text{H})_m-\text{H} \]

wherein R is an aliphatic radical and n is from about 0 to about 15.

In another embodiment, a method for treating asphalt comprises adding a hydrogen sulfide scavenger composition to the asphalt products, wherein the hydrogen sulfide scavenger composition comprises a polyaliphatic amine having the formula I:

\[ \text{H}_2\text{NRNH}-(\text{R}_n\text{H})_m-\text{H} \]

wherein R is an aliphatic radical and n is from about 0 to about 15.

In another embodiment, a hydrogen sulfide scavenger composition comprises a polyaliphatic amine and a catalyst, said polyaliphatic amine having the formula I:

\[ \text{H}_2\text{NRNH}-(\text{R}_n\text{H})_m-\text{H} \]

wherein R is an aliphatic radical and n is from about 0 to about 15.

The various embodiments provide an organic based hydrogen sulfide scavenger for asphalt and for an improved method of removing hydrogen sulfide from asphalt products.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a bar graph showing the amount of hydrogen sulfide in ppm in asphalt samples versus time in minutes.

FIG. 2 is a bar graph showing the amount of hydrogen sulfide in ppm in asphalt samples versus time in minutes.

DETAILED DESCRIPTION OF THE INVENTION

The singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. The endpoints of all ranges reciting the same characteristic are independently combinable and inclusive of the recited endpoint. All references are incorporated herein by reference.

The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., includes the tolerance ranges associated with measurement of the particular quantity).

“Optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, or that the subsequently identified material may or may not be present, and that the description includes instances where the event or circumstance occurs or where the material is present, and instances where the event or circumstance does not occur or the material is not present.

In one embodiment, a method for reducing hydrogen sulfide in asphalt, comprises adding a hydrogen sulfide scavenger composition to the asphalt, wherein the hydrogen sulfide scavenger composition comprises a polyaliphatic amine having formula I:

\[ \text{H}_2\text{NRNH}-(\text{R}_n\text{H})_m-\text{H} \]

wherein R is an aliphatic radical and n is from about 0 to about 15.

Asphalt products often contain hydrogen sulfide, which is corrosive and poisonous and must be removed before the asphalt products can be upgraded to higher value products, such as gasoline and diesel. Asphalt is any type of crude oil residuum or heavy oil that is produced from the distillation of crude oil. It is a heavy intermediate or finished product having a boiling point in a temperature range from about 500°F to about 1100°F. The asphalt can have a range of hydrogen sulfide content and any level of hydrogen sulfide can be treated.

The hydrogen sulfide scavenger controls and removes hydrogen sulfide from asphalt. It is an organic-based composition comprising a polyaliphatic amine. The polyaliphatic amine has the formula I:

\[ \text{H}_2\text{NRNH}-(\text{R}_n\text{H})_m-\text{H} \]

wherein R is an aliphatic radical and n is from about 0 to about 15.

In one embodiment, a is from about 0 to about 10. In another embodiment, n is from about 1 to about 5.

In one embodiment, the aliphatic radical may be alkyl, alkenyl or alkoxyl. The aliphatic radical may be a straight or branched chain and may be substituted or unsubstituted. In one embodiment, the aliphatic group is substituted with one or more organic or inorganic radicals, such as halogen, alkyl, alkenyl, amino, hydroxyl, cyano and mercapto groups. In one embodiment, the halogen group may be chloro, bromo or iodo.

In another embodiment, the aliphatic group is a C1-C30 alkyl group, a C2-C30 alkenyl group or a C1-C30 alkoxyl group. In one embodiment, the alkyl group may be methyl, ethyl, n-butyl, t-butyl, isopropyl, pentyl or hexyl. In another embodiment, the alkoxyl group is methoxy, ethoxy or
isopropoxy. In another embodiment, the alkenyl group may be ethylene, methylethylene, trimethylene, phenylethylene or propylene.

In one embodiment, the polyaliphatic amine is a polyalkyleneamine. In another embodiment, the polyalkyleneamine may be ethylenediamine, diethylenetriamine, triethylenetetraamine, tetraethylenepentamine, propylenediamine, propylenediamine, tetraethylpentamine, hexaethyleneptamine, heptamethyleneptamine, octaethylbenzenediamine, nonaethylenedecamine, decaethyleneundecamine, dodecaethyleneundecamine, tridecaethyleneundecamine, dodecaethylenetetradecamine, tridecaethylenetetradecamine, dodecaethylenetetradecamine or N-tallow propylenediamine.

The scavenger composition is added to the asphalt in any conventional manner. In one embodiment, the scavenger composition is injected into the asphalt, such as via a metering pump system. The scavenger composition can be injected into the asphalt in a continuous manner or can be added in one or more batch modes and repeated additions may be made.

The scavenger composition is added to the asphalt in an amount sufficient to reduce the levels of hydrogen sulfide in the asphalt. In one embodiment, the scavenger composition is added in an amount of from about 50 ppm to about 3000 ppm by weight, based on the weight of the asphalt. In another embodiment, the scavenger composition is added in an amount of from about 50 ppm to about 1000 ppm by weight, based on the weight of the asphalt.

The scavenger composition significantly reduces the hydrogen sulfide levels contained in the asphalt. The actual amount of residual hydrogen sulfide will vary depending on the starting amount. In one embodiment, the hydrogen sulfide levels are reduced to 10 ppm by weight or less, based on the weight of the asphalt. In another embodiment, the hydrogen sulfide levels are reduced to 2 ppm by weight or less, based on the weight of the asphalt. In another embodiment, the hydrogen sulfide levels are reduced to less than 1 ppm by weight, based on the weight of the asphalt.

The hydrogen sulfide scavenger composition may optionally include a solvent. The solvent aids the scavenger composition in dispersing with the asphalt products. The solvent may be any solvent that is miscible with polyaliphatic amines and that has a high flashpoint. In one embodiment, the solvent has a flashpoint of at least 200°F. In one embodiment, the solvent includes, but is not limited to, propylene glycol, 1,4-butanediol, ethylene carbonate or propylene carbonate.

In one embodiment, the solvent may be added in an amount of from about 0 to about 300 percent by weight based on the weight of the polyaliphatic amine. In another embodiment, the solvent is added in an amount of from about 0 to about 150 percent by weight based on the weight of the polyaliphatic amine. In another embodiment, the solvent is added in an amount of from about 0 to about 80 percent by weight, based on the weight of the polyaliphatic amine.

In another embodiment, the hydrogen sulfide scavenger composition comprises a polyaliphatic amine and a catalyst. The catalyst improves the efficacy of the scavenger composition and enhances removal of hydrogen sulfide. The catalyst may be any suitable quaternary ammonium salt. In one embodiment, the catalyst has formula II:

R_1R_2R_3R_4NX

wherein R_1, R_2, R_3 and R_4 are each independently alkyl groups having from 1 to 30 carbon atoms, hydroxyalkyl groups having from 1 to 30 carbon atoms or an aryl group having from 6 to 30 carbon atoms; and X is a halide or methyl sulfate. In one embodiment, the halide may be chloride, bromide or iodide. In another embodiment, the catalyst is alkyl benzyl ammonium chloride or benzyl cocaokyl dimethyl quaternary ammonium chloride. In another embodiment, the catalyst includes, but is not limited to dicocodimethylammonium chloride, distallowdimethylammonium chloride, dihydrogenated tallow alkyl dimethyl quaternary ammonium methyl chloride, methyl bis[2-hydroxyethyl] cocaokyl quaternary ammonium chloride, dimethyl[2-ethyl] tallow ammonium methyl sulfate or hydrogeanated tallow alkyl (2-ethylhexyl) dimethyl quaternary ammonium methylsulfate.

In one embodiment, a scavenger composition comprises from about 20 to about 98 percent by weight polyaliphatic amine, from about 2 to about 20 percent by weight catalyst and from about 0 to about 78 percent by weight of a solvent, based on the weight of the composition. In another embodiment, the scavenger composition comprises from about 50 to about 97 percent by weight polyaliphatic amine, from about 3 to about 10 percent by weight catalyst and from about 0 to about 47 percent by weight of a solvent, based on the weight of the composition.

The scavenger composition may optionally contain other compounds, such as amine dispersants, corrosion inhibitors, surfactants and the like. In one embodiment, the surfactants include anionic surfactants, nonionic surfactants or combinations thereof.

The scavenger composition may be added to the asphalt as one formulation of the polyaliphatic amine and other components may be added separately to the asphalt. Optional components, such as the catalyst, solvent or other additives may be added separately, may be combined into one formulation with the polyaliphatic amine or may be preblended with other components before adding to the asphalt. In one embodiment, the components in the scavenger composition are blended together before adding to the asphalt.

In another embodiment, a method for treating asphalt comprises adding a hydrogen sulfide scavenger composition to the asphalt products, wherein the hydrogen sulfide scavenger composition comprises a polyaliphatic amine having formula I:

H_2NRNH—(RNNH)_n—H

wherein R is an aliphatic radical and n is from about 0 to about 15.

In one embodiment, n is from about 0 to about 10. In another embodiment, n is from about 1 to about 5.

In one embodiment, the aliphatic radical may be alkyl, alkenyl or alkoxyl. The aliphatic radical may be a straight or branched chain and may be substituted or unsubstituted. In one embodiment, the aliphatic group is substituted with one or more organic or inorganic radicals, such as halogen, alkyl, alkoxy, amino, hydroxyl, cyano and mercapto groups. In one embodiment, the halogen group may be chloro, bromo or iodo.

In another embodiment, the aliphatic group is a C_1-C_30 alkyl group, a C_1-C_30 alkenyl group or a C_1-C_30 alkoxyl group. In one embodiment, the alkyl group may be methyl, ethyl, n-butyl, t-butyl, isopropyl, pentyl or hexyl. In another embodiment, the alkoxy group is methoxy, ethoxy or...
isopropoxy. In another embodiment, the alkenyl group may be ethylene, methylethylene, trimethylene, phenylethylene or propylene.

[0041] In one embodiment, the polyalkylenamine is a polyalkyleneamine. In another embodiment, the polyalkyleneamine may be ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, propylenediamine, tetrabutylenepentamine, hexaethylenepentamine, hexapentylenetetramine, heptaethylenoctamine, octaethylbenzyl ammonium chloride (ARQUAD DMCB-80 from Akzo-Nobel) in 34 mg propylene glycol. Sample 2 was added to 578 g of an asphalt (from Conoco Phillips, West Lake, La. refinery) containing over 350 ppm hydrogen sulfide. Sample 2 was added to 821 g of the asphalt. The concentration of the hydrogen sulfide in the vapor phase was determined at frequent intervals as shown in FIG. 1. The data scatter can be attributed to a +/-15% error in determining H₂S vapor concentrations.

[0051] FIG. 1 shows that samples 1 and 2 reduce and control the hydrogen sulfide content in the asphalt. The addition of the catalyst (alkyl benzyl ammonium chloride) significantly increases the efficacy of the scavenger composition. Sample 2 effectively controls the hydrogen sulfide level in 42% more asphalt.

Example 2

A control sample A was prepared by dispersing 51 mg of 1,3,5-trimethylhexahydro-1,3,5-triazine in 34 mg propylene glycol. A control sample B was prepared by dispersing 51 mg of MA-triazine and 3 mg of alkyl benzyl ammonium chloride (ARQUAD DMCB-80 from Akzo-Nobel) in 34 mg propylene glycol. Control sample A was added to 578 g of an asphalt (from Conoco Phillips, West Lake, La. refinery) containing over 350 ppm hydrogen sulfide. Control sample B was added to 821 g of the asphalt. The concentration of the hydrogen sulfide in the vapor phase was determined at frequent intervals as shown in FIG. 2. The data scatter can be attributed to a +/-15% error in determining H₂S vapor concentrations.

[0053] FIG. 2 shows that the catalyst (ARQUAD DMCB-80) has no impact on the efficacy of hydrogen sulfide scavenging when using an organic-based MA-Triazine. The data in FIG. 2 also shows that the overall scavenging of the control sample is not as effective as the scavenging for samples 1 and 2 in FIG. 1.

[0054] While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope herein. Accordingly, various modifications, adaptations and alternatives may occur to one skilled in the art without departing from the spirit and scope herein.

What is claimed is:

1. A method for reducing hydrogen sulfide in asphalt, comprising adding a hydrogen sulfide scavenger composition to the asphalt, wherein the hydrogen sulfide scavenger comprises a polyalkylenamine having formula 1:

$$H_2NR(NH)_{n-1}H$$

wherein R is an aliphatic radical and n is from about 0 to about 15.

2. The method of claim 1, wherein the aliphatic radical is a C₁-C₃₀ alkyl, C₂-C₃₀ alkenyl or C₁-C₃₀ alkynyl.

3. The method of claim 1, wherein the polyalkylenamine is a polyalkyleneamine.

4. The method of claim 3, wherein the polyalkyleneamine is selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, propylenediamine, tetrabutylenepentamine, hexaethylenepentamine, hexapentylenetetramine, heptaethylenoctamine, octaethylbenzyl ammonium chloride (ARQUAD DMCB-80 from Akzo-Nobel) in 34 mg propylene glycol. Sample 1 was added to 578 g of an asphalt (from Conoco Phillips, West Lake, La. refinery) containing over 350 ppm hydrogen sulfide. Sample 2 was added to 821 g of the asphalt. The concentration of the hydrogen sulfide in the vapor phase was determined at frequent intervals as shown in FIG. 1. The data scatter can be attributed to a +/-15% error in determining H₂S vapor concentrations.

[0051] FIG. 1 shows that samples 1 and 2 reduce and control the hydrogen sulfide content in the asphalt. The addition of the catalyst (alkyl benzyl ammonium chloride) significantly increases the efficacy of the scavenger composition. Sample 2 effectively controls the hydrogen sulfide level in 42% more asphalt.

Example 2

A control sample A was prepared by dispersing 51 mg of 1,3,5-trimethylhexahydro-1,3,5-triazine in 34 mg propylene glycol. A control sample B was prepared by dispersing 51 mg of MA-triazine and 3 mg of alkyl benzyl ammonium chloride (ARQUAD DMCB-80 from Akzo-Nobel) in 34 mg propylene glycol. Control sample A was added to 578 g of an asphalt (from Conoco Phillips, West Lake, La. refinery) containing over 350 ppm hydrogen sulfide. Control sample B was added to 821 g of the asphalt. The concentration of the hydrogen sulfide in the vapor phase was determined at frequent intervals as shown in FIG. 2. The data scatter can be attributed to a +/-15% error in determining H₂S vapor concentrations.
undecaethylenedodecamine, dodecaethylenetridecamine, tridecaethylenedodecamine, dodecaethylenetriamine, tridecaethylenetedractamaine and N-tallow propylenediamine.

5. The method of claim 1, wherein the scavenger composition is added in an amount of from about 50 ppm to about 3000 ppm by weight, based on the weight of the asphalt.

6. The method of claim 1, wherein the hydrogen sulfide scavenger composition further comprises a solvent.

7. The method of claim 1, wherein the hydrogen sulfide scavenger composition further comprises a catalyst.

8. The method of claim 7, wherein the catalyst has formula II:

$$R_1R_2R_3R_4N\times$$

wherein $R_1$, $R_2$, $R_3$ and $R_4$ are each independently alkyl groups having from 1 to 20 carbon atoms, hydroxalkyl groups having from 1 to 20 carbon atoms or an aryl group having from 6 to 20 carbon atoms; and X is a halide or methyl sulfite.

9. The method of claim 8, wherein the catalyst is selected from the group consisting of dicyclopentadienylmethylammonium chloride, dichlorodiethylaminomethylammonium chloride, di(hydrogenated tallow alkyl) dimethyl quaternary ammonium methyl chloride, methyl bis(2-hydroxyethyl) cocokyl quaternary ammonium chloride, dimethyl(2-ethyl) tallow ammonium methyl sulfite and hydrogenated tallow alkyl(2-ethyl)dimethyl quaternary ammonium methylsulfate.

10. The method of claim 7, wherein the scavenger composition comprises from about 20 to about 98 percent by weight polyaliphatic amine, from about 2 to about 20 percent by weight catalyst and from 0 to about 78 percent by weight of a solvent, based on the weight of the composition.

11. A method for treating asphalt comprising adding a hydrogen sulfide scavenger composition to the asphalt products, wherein the hydrogen sulfide scavenger composition comprises a polyaliphatic amine having the formula I:

$$R\times_{\text{N}}$$

wherein R is an aliphatic radical and n is from about 0 to about 15.

12. The method of claim 11, wherein the aliphatic radical is a C$_1$-C$_{15}$ alkyl, C$_2$-C$_{15}$ alkenyl or C$_3$-C$_{30}$ alkoxy.

13. The method of claim 11, wherein the polyaliphatic amine is a polyalkyleneamine.

14. The method of claim 13, wherein the polyalkyleneamine is selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, propylenediamine, tetrabutylpentamine, hexaethylenepentamine, hexaethylhexamine, heptamethyleneamine, octamethyleneamine, nonaethylenenedecamaine, decaethylenenedecamine, decaethyleneundecamine, undecaethylenenedecadecamine, dodecaethylenetetradecamine, tridecaethylenetedractamaine and N-tallow propylenediamine.

15. The method of claim 11, wherein the scavenger composition is added in an amount of from about 50 ppm to about 3000 ppm by weight, based on the weight of the asphalt.

16. The method of claim 11, wherein the hydrogen sulfide scavenger composition further comprises a solvent.

17. The method of claim 11, wherein the hydrogen sulfide scavenger composition further comprises a catalyst.

18. The method of claim 17, wherein the catalyst has formula II:

$$R_1R_2R_3R_4N\times$$

wherein $R_1$, $R_2$, $R_3$ and $R_4$ are each independently alkyl groups having from 1 to 30 carbon atoms, hydroxyalkyl groups having from 1 to 30 carbon atoms or an aryl group having from 6 to 30 carbon atoms; and X is a halide or methyl sulfite.

19. The method of claim 18, wherein the catalyst is selected from the group consisting of dicyclopentadienylmethylammonium chloride, dichlorodiethylaminomethylammonium chloride, di(hydrogenated tallow alkyl) dimethyl quaternary ammonium methyl chloride, methyl bis(2-hydroxyethyl) cocokyl quaternary ammonium chloride, dimethyl(2-ethyl) tallow ammonium methyl sulfite and hydrogenated tallow alkyl(2-ethyl)dimethyl quaternary ammonium methylsulfate.

20. The method of claim 17, wherein the scavenger composition comprises from about 20 to about 98 percent by weight polyaliphatic amine, from about 2 to about 20 percent by weight catalyst and from 0 to about 78 percent by weight of a solvent, based on the weight of the composition.

21. A hydrogen sulfide scavenger composition comprising a polyaliphatic amine and a catalyst, said polyaliphatic amine having the formula I:

$$R\times_{\text{N}}$$

wherein R is an aliphatic radical and n is from about 0 to about 15.

22. The scavenger composition of claim 21, wherein the polyaliphatic amine is a C$_1$-C$_{30}$ alkyl, C$_2$-C$_{30}$ alkenyl or C$_3$-C$_{30}$ alkoxy.

23. The scavenger composition of claim 21, wherein the polyaliphatic amine is a polyalkyleneamine.

24. The scavenger composition of claim 23, wherein the polyalkyleneamine is selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, propylenediamine, tetrabutylpentamine, hexaethylenepentamine, hexaethylhexamine, heptamethyleneamine, octamethyleneamine, nonaethylenenedecamaine, decaethylenenedecamine, decaethyleneundecamine, undecaethylenenedecadecamine, dodecaethylenetetradecamine, tridecaethylenetedractamaine and N-tallow propylenediamine.

25. The scavenger composition of claim 21, wherein the catalyst has formula II:

$$R_1R_2R_3R_4N\times$$

wherein $R_1$, $R_2$, $R_3$ and $R_4$ are each independently alkyl groups having from 1 to 30 carbon atoms, hydroxyalkyl groups having from 1 to 30 carbon atoms or an aryl group having from 6 to 30 carbon atoms; and X is a halide or methyl sulfite.

26. The scavenger composition of claim 25, wherein the catalyst is selected from the group consisting of dicyclopentadienylmethylammonium chloride, dichlorodiethylaminomethylammonium chloride, di(hydrogenated tallow alkyl) dimethyl quaternary ammonium methyl chloride, methyl bis(2-hydroxyethyl) cocokyl quaternary ammonium chloride, dimethyl(2-ethyl) tallow ammonium methyl sulfite and hydrogenated tallow alkyl(2-ethyl)dimethyl quaternary ammonium methylsulfate.

27. The scavenger composition of claim 21, wherein the composition further comprises a solvent.

28. The scavenger composition of claim 27, wherein the scavenger composition comprises from about 20 to about 98 percent by weight polyaliphatic amine, from about 2 to about 20 percent by weight catalyst and from 0 to about 78 percent by weight of a solvent.
by weight of a solvent, based on the weight of the composition.

29. The method of claim 7 wherein the polyaliphatic amine is diethylene triamine and the catalyst is alkyl benzyl ammonium chloride.

30. The method of claim 29 wherein the scavenger composition further comprises a solvent having a flashpoint of at least about 200°F.

* * * * *