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(54) **METHODS AND COMPOSITIONS FOR REMOVING SULFUR FROM LIQUID HYDROCARBONS USING AMMONIUM ADDUCTS**

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(57) **ABSTRACT**

Improved desulfurization compositions are provided for removing substantial fractions of sulfur, sulfur complexes, and sulfur compounds from liquid hydrocarbons such as crude oil and fuels. The preferred compositions comprise amine adducts, such as the adduct formed by reacting benzoic acid and a fatty acid amine. The compositions may be contacted with liquid hydrocarbons in the presence of water to achieve high levels of desulfurization. Preferably, the compositions are added substantially continuously to a flowing stream of liquid hydrocarbon and water, e.g., to the output from a producing oil well or in pipeline transmission and/or refinery equipment.

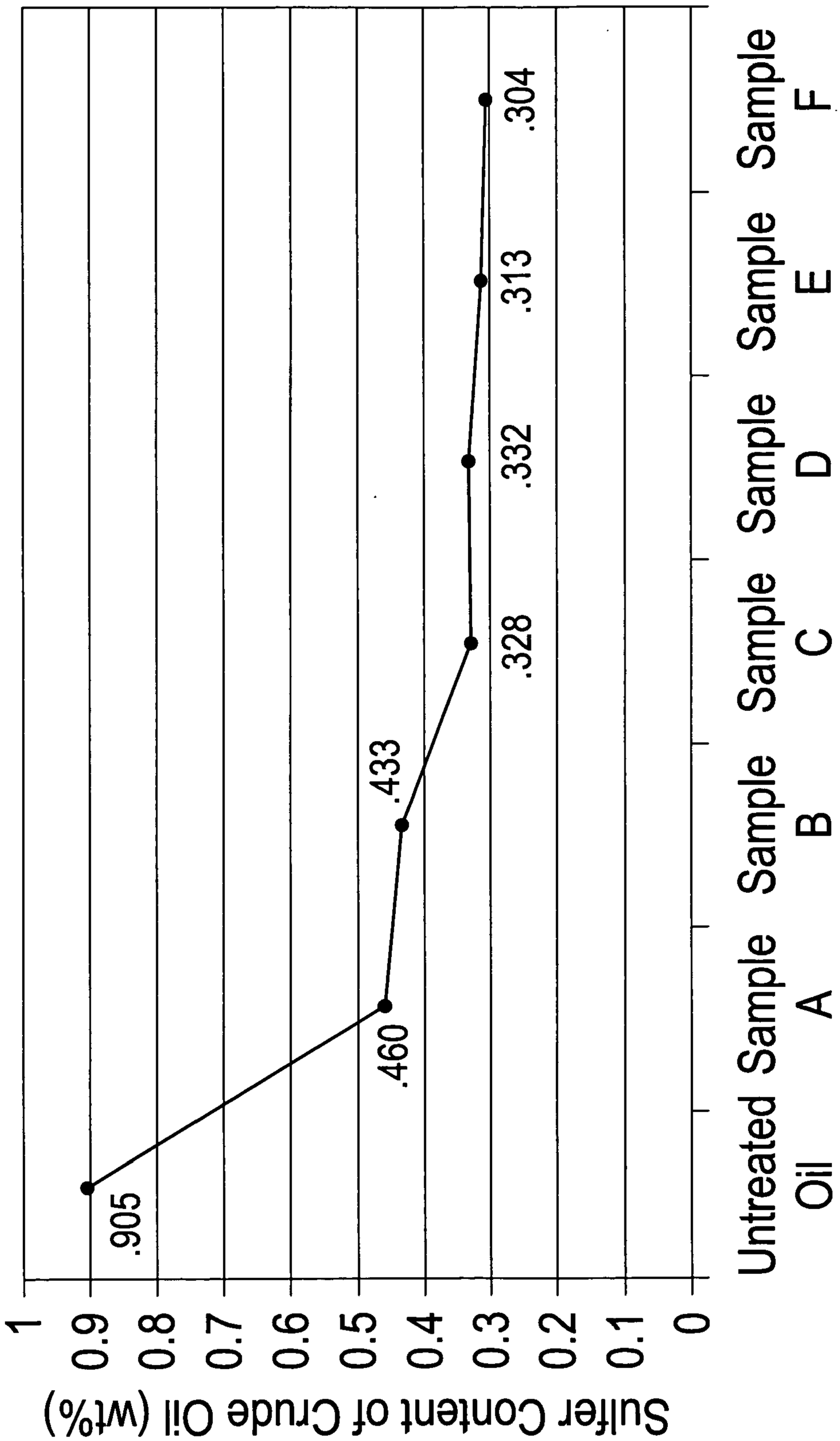
Sulfer Content of Crude Oil (wt%)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
.905
.433
.460
.328
.313
.304
.332
Untreated Sample Oil A
Sample B
Sample C
Sample D
Sample E
Sample F

Fig. 1.

METHODS AND COMPOSITIONS FOR REMOVING SULFUR FROM LIQUID HYDROCARBONS USING AMMONIUM ADDUCTS

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention is broadly concerned with desulfurization of liquid hydrocarbon/water mixtures such as crude oils and derivatives thereof. More particularly, the invention is concerned with compositions which can be directly contacted with liquid hydrocarbons and water to effect substantial desulfurization of the hydrocarbon fractions thereof, as well as methods of preparing and using the compositions. The compositions of the invention preferably are made up of solid or liquid materials including therein an amine adduct such as the adduct derived from the reaction of coco-1,3-diaminopropane and an acid such as benzoic acid.

[0003] 2. Description of the Prior Art

[0004] The concentration of sulfur in crude oil is typically between 0.05 and 5.0% (by weight), although values as high as 13.95% have been reported. In general, the distribution of sulfur in crude oil is such that the proportion of sulfur increases along with the boiling point of the distillate fraction. As a result, the higher the boiling range of the fuel the higher the sulfur content will tend to be. For example, a middle-distillate-range fraction, e.g., diesel fuel, will typically have a higher sulfur content than the lower-boiling-range gasoline fraction. Upon combustion, the sulfur in fuels can contribute to air pollution in the form of particulate material and acidic gases, such as sulfur dioxide. To reduce sulfur-related air pollution, the level of sulfur in fuels is regulated, and to meet these regulations sulfur must be removed from fuels during the refining process.

[0005] Refineries remove organic sulfur from crude oil-derived fuels by hydrodesulfurization (HDS). HDS is a catalytic process that converts organic sulfur to hydrogen sulfide gas by reacting crude oil fractions with hydrogen at pressures between 150 and 3,000 lb/in^2 and temperatures between 290 and 455° C., depending upon the feed and level of desulfurization required. Organic sulfur compounds in the lower-boiling fractions of petroleum, e.g., the gasoline range, are mainly thiols, sulfides and thiophenes, which are readily removed by HDS. However, middle-distillate fractions, e.g., the diesel and fuel oil range, contain significant amounts of benzothiophenes and dibenzothiophenes (DBTs), which are considerably more difficult to remove by HDS. Among the most refractory of these compounds are DBTs with substitutions adjacent to the sulfur moiety. Compounds of this type are referred to as sterically hindered compounds because the substitutions are believed to sterically hinder access of the sulfur atom to the catalyst surface. Due to their resistance to HDS, sterically hindered compounds represent a significant barrier to reaching very low sulfur levels in middle- and heavy-distillate-range fuels. The high cost and inherent chemical limitations associated with HDS make alternatives to this technology of interest to the petroleum industry. Moreover, current trends toward stricter regulations on the content of sulfur in fuels provide incentive for the continued search for improved desulfurization processes.

[0006] Biodesulfurization has been studied as an alternative to HDS for the removal of organic sulfur from fuels. The use of hydrocarbon degradation pathways that attached DBT were unsuccessful because these systems relied on the oxidation and mineralization of the carbon skeleton instead of on sulfur removal and therefore significantly reduced the fuel value of the desulfurized end product. More recently, bacteria that desulfurize DBT and a variety of other organic sulfur compounds typically found in petroleum oils via a sulfur selective oxidative pathway that does not remove carbon have been isolated. This pathway involves the sequential oxidation of the sulfur moiety followed by cleavage of the carbon sulfur bonds.

[0007] Amine salts such as those formed by the reaction between acetic or acrylic acids and coco-1,3-diaminopropane have been used in the past as corrosion inhibitors or biocides in producing wells. Such salts are typically added in large amounts on an infrequent basis to producing wells to "shock" the system and serve as an effective biocide, or in very small quantities for corrosion inhibition purposes. In addition, amine salt corrosion inhibitors are commonly used with emulsion breakers, in order to minimize any oil-water emulsions which can interfere with effective inhibition. See, e.g., U.S. Pat. No. 5,427,999. Additional references include: U.S. Pat. Nos. 4,297,237; 5,322,630; 2,995,603; 3,996,024; 5,019,361; 4,131,583; 5,032,318; 4,248,717; 4,490,155; 4,290,900; 4,157,972; 4,011,882; 4,499,006; U.S. Patent Publication No. U.S. 2003/0200697; EPO Publications 256802 and 798364; and Japanese Publication No. EP97302039.

[0008] Despite all of these well-known desulfurization efforts, there still exists a need for easy and cost-effective desulfurization of liquid hydrocarbons, using readily available components and a simplified removal mechanism.

SUMMARY OF THE INVENTION

[0009] The present invention overcomes the problems outlined above and provides compositions effective for desulfurization of liquid hydrocarbons. As used herein, desulfurization or removal of sulfur from hydrocarbons refers to the removal of any or all types of sulfur and sulfur-bearing species, e.g., elemental sulfur, sulfur complexes and the full gamut of sulfur compounds found in hydrocarbons such as mercaptans and thiophenes.

[0010] As used herein, "alkyl," whether referring to individual compounds or as moieties of larger compounds, is intended to embrace both saturated and unsaturated species such as alkenyl and alkynyl compounds or groups, as well as straight and branched chain compounds and species. Similarly, "aryl" is intended to embrace mono- or poly-ring compounds or moieties.

[0011] Broadly speaking, the treatment compositions of the invention include adducts of secondary, tertiary, or quaternary mono- and polyamines and mixtures thereof. Preferred amines are of the formula:

$$R—(NR_1—(CH_2)_n—NHR_2)_x$$

wherein R is selected from the group consisting of aryl, alkyl, cycloalkyl, arylalkyl, alkoxyalkyl, hydroxyalkyl, and alkoxyhydroxy groups and wherein the alkyl groups or moieties are selected from the C2-C24 alkyls, R_1 and R_2 are individually selected from the group consisting of H and

C1-C4 alkyls, n is from about 2-12, and x is from about 1-8. The most preferred amines for use in the invention are the C8-C24 fatty acid diamines such as cocodiamine and tallowdiamine.

[0012] The amines of the invention are reacted with an appropriate acid in order to yield the adducts of the invention. A wide variety of acids can be used in this context, but generally the acids employed should not be sulfur-bearing. Exemplary acids include C2-C8 alkyl and aryl mono- and polyorganic acids and derivatives thereof (e.g., acetic, propionic, hydroacetic, adipic, succinic, benzoic) and inorganic acids (e.g., hydrohalo, boric). The adduct-forming reaction is normally very straightforward, involving mixing together the respective components and creating the resultant adduct. Many such reactions are slightly exothermic.

[0013] The adducts of the invention can be used in either solid (e.g., pellets, balls, sticks, or powders) or liquid dispersion form. In the case of solids, the adduct(s) can be mixed using a high intensity mixing device, followed by forming discrete, solid bodies. If desired, a minor amount of an anti-caking agent may be added to facilitate handling, e.g., up to about 5% (and usually no more than about 1%) by weight of an agent such as sodium silico aluminate, based upon the total weight of the composition exclusive of anti-caking agent taken as 100% by weight. For ease of use, however, the amine adducts of the invention are normally dispersed in water or other aqueous liquids, typically at a level of from about 1-2.5 lbs. of the solid adduct(s) per gallon of aqueous liquid. Normally, the adducts are readily dispersible in aqueous systems using only moderate mixing.

DRAWING

[0014] The single FIGURE is a graph summarizing a series of tests using preferred amine adducts of the invention for desulfurization of crude oil.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0015] The amine adducts of the invention, whether in solid or liquid form, are capable of effecting a substantial desulfurization of liquid hydrocarbons. The hydrocarbons may be of virtually any type, for example crude oil and fuels derived from crude oil such as all grades of diesel fuel, jet fuels, and gasolines. However, it is normally desired to treat crude oil using the amine adducts of the invention to thereby lessen the sulfur loading on downstream refinery processes. Broadly speaking, the amine adducts of the invention are contacted with a selected liquid hydrocarbon in an effective amount to achieve desulfurization, in the presence of water. The water may be a part of a hydrocarbon-water mixture as in the case of a producing well output, or the water fraction may be added along with the adduct. The amine adducts should be contacted with liquid hydrocarbons at a level of from about 100-50,000 ppm (more preferably from about 250-20,000 ppm or 250-10,000 ppm, and most preferably from about 300-2,000 ppm) amine adduct per ppm of total sulfur in the liquid hydrocarbon.

[0016] In the case of crude oil, contact between the amine adducts of the invention and the crude can most advantageously be made simply by dropping or injecting the amine adduct material directly into a producing well, and specifically into the annulus and/or producing zone of the well. A recycled side stream of well fluid is also injected which helps assure that the amine adducts reach the bottom of the well. Normally, downhole temperatures are greater than ambient surface temperatures, and it has been found that such higher temperatures accelerate the desired desulfurization. The unwanted sulfur material is separated into the water phase of the well fluid and can thus be readily handled and disposed of by conventional means.

[0017] In other treatment applications such as in well field tanks and separators, and in transmission pipelines and in refinery processing, the amine adducts are added to the liquid hydrocarbons with mixing, if possible, such as through the use of static mixers, agitators, or ultrasound treatment. Where possible, elevated temperatures of from about 100-180° F., more preferably from about 120-160° F., should be achieved during contact between the amine adducts and the liquid hydrocarbons, e.g., the liquid hydrocarbon should be heated to these levels.

[0018] In preferred forms, the amine adduct desulfurization compositions are added during pipeline transport and/or refinery treatment of a liquid hydrocarbon. In this context, the compositions may be added at one instance, substantially continuously or at less frequent intervals. In another preferred method, the compositions of the invention are added to a producing well for desulfurization of crude. In this mode of use, the compositions are added substantially continuously, e.g., by continuously metering an appropriate amount of the desulfurization composition into the well. As used herein, however, "substantially continuously" with reference to addition of desulfurization composition(s) is intended to embrace continuous metering as described as well as less frequent additions, but typically at least twice per day.

[0019] In all instances, however, the adducts of the invention should be contacted with the liquid hydrocarbon in the presence of water. Water should be present at a level of at least about 1% by weight, and more preferably at least about 5% by weight. Considering the situation where a water-hydrocarbon mixture is treated, the hydrocarbon fraction should be present at a level of at least about 50% by weight, and more preferably at least about 80% by weight. In particularly preferred forms, the hydrocarbon and water fractions form a hydrocarbon-water emulsion.

[0020] The presence of water with the hydrocarbon in the methods of the invention is believed to facilitate removal of sulfur from the hydrocarbon and to partially solubilize the sulfur in the water. Indeed, attempts to use the adducts of the invention in the absence of water have generally given very poor desulfurization results.

[0021] The compositions and methods of the invention can commonly achieve desulfurization by removal of elemental sulfur, sulfur complexes, and/or sulfur-bearing compounds such as thiophenes; levels of sulfur reduction of at least about 25%, and more preferably from about 40-70%, can be obtained.

EXAMPLE 1

[0022] In this example, a preferred amine adduct was prepared and used to desulfurize Saudi crude oil having a sulfur content of 3.16%.

[0023] The amine adduct was prepared by mixing together 20% by weight of solid benzoic acid and 80% by weight of

liquid coco-1,3-diaminopropane, followed by moderate mixing. The reaction was slightly exothermic. Next, 2.5 gms. of the resultant adduct product were added to 30 ml. of water, and this aqueous dispersion was added to 120 ml. of Saudi crude oil. The oil/aqueous adduct mixture was then placed in a separatory funnel which was shaken vigorously approximately 100 times. The hydrocarbon and aqueous phases were then allowed to separate, and the hydrocarbon fraction was drawn off and analyzed to determine total sulfur content. The treated hydrocarbon fraction exhibited a sulfur content of 2.32%, constituting a 26.5% sulfur reduction.

EXAMPLE 2

[0024] The desulfurization test of Example 1 was repeated using 6 additional amine adduct products. Specifically, each amine adduct was prepared by reacting coco-1,3-diaminopropane with glacial acetic acid (Sample A), propionic acid (Sample B), boric acid (Sample C), hydroacetic acid (Sample D), adipic acid (Sample E), and succinic acid (Sample F). The respective samples were dispersed in 30 ml. water, and the resulting dispersions were added to 120 ml. of Alaskan crude oil. The above-described separatory funnel treatment was then carried out on each oil sample.

[0025] The results of this series of tests are set forth in FIG. **1**. As illustrated, the untreated oil had a sulfur content of 0.905% and the treatment according to the invention resulted in a reduction in sulfur content of from about 49.2 to 66.4%.

EXAMPLE 3

[0026] In this example, Alaskan crude oil having a sulfur content of 0.894% was mixed with distilled water at varying percentages, and the resulting mixtures were each treated with 25 gms. of the amine-benzoic acid composition of Example 1 in 100 ml. of water. The test protocol of Example 1 was then carried out on each sample, giving the following results:

Oil (ml)	Water (ml)	Aliquot (ml)	Mixing Temp (° F.)	Sulfur Content (wt. %)	% Sulfur Reduction
120	0	10	120	0.340	62
120	10	10	120	0.235	73.7
120	20	10	120	0.525	41.3
120	30	10	120	0.252	71.8
120	50	10	120	0.232	74.0

We claim:

1. A method of reducing the content of sulfur and/or sulfur-bearing compounds in liquid hydrocarbon during pipeline transport and/or refining thereof, said method comprising the step of contacting the hydrocarbon with an effective amount of a desulfurization composition and in the presence of water during said pipeline transfer and/or said refining, said composition comprising the adduct reaction product of an amine and an acid, and separating some of the sulfur or sulfur-bearing compounds from said liquid hydrocarbon.

2. The method of claim 1, said amine adduct selected from adducts of amines of the formula

$$R—(NR_1—(CH_2)_n—NHR_2)_x$$

where R is selected from the group consisting of aryl, alkyl, cycloalkyl, arylalkyl, alkoxyalkyl, hydroxyalkyl, and alkoxyhydroxy groups and wherein the alkyl groups or moieties are selected from the C2-C24 alkyls, R_1 and R_2 are individually selected from the group consisting of H and C1-C4 alkyls, n is from about 2-12, and x is from about 1-8

3. The method of claim 2, said adduct comprising the reaction product of a fatty acid amine and an acid.

4. The method of claim 3, said fatty acid amine being a C8-C24 fatty acid amine.

5. The method of claim 4, said fatty acid amine being coco-1,3-diaminopropane.

6. The method of claim 3, said acid comprising benzoic acid.

7. The method of claim 1, said composition being in the form of an aqueous dispersion.

8. The method of claim 7, said aqueous dispersion comprising of from about 1-1.5 lbs. of said composition per gallon of aqueous liquid.

9. The method of claim 1, said composition being contacted with said liquid hydrocarbon at a level of from about 100-50,000 ppm of the adduct per ppm of total sulfur in the liquid hydrocarbon.

10. The method of claim 9, said level being from about 250-10,000 ppm.

11. The method of claim 10, said level being from about 300-2,000 ppm.

12. The method of claim 1, said composition consisting essentially of said adduct.

13. The method of claim 1, said hydrocarbon being in a flowing stream with water, said method including the step of substantially continuously metering amounts of said composition into said flowing stream.

14. The method of claim 1, said liquid hydrocarbon and water forming an oil-water emulsion, said composition being added to said emulsion.

15. The method of claim 1, said hydrocarbon being mixed with water to form a mixture, said mixture comprising at least about 50% by weight liquid hydrocarbon.

16. The method of claim 15, said mixture comprising at least about 80% by weight liquid hydrocarbon.

17. A method of reducing the content of sulfur and/or sulfur bearing compounds in crude oil during operation of a crude oil well yielding a mixture including crude oil and water, comprising the steps of substantially continuously adding a desulfurization composition into the well during said operation thereof, said composition comprising an adduct derived from the reaction between an amine and an acid, and separating at least a portion of said water from said liquid hydrocarbon after said addition step.

18. The method of claim 17, said composition being added by substantially continuously metering the composition into the well.

19. The method of claim 17, said composition being added intermittently to the well, with a frequency of at least twice per day.

20. The method of claim 17, said adduct selected from adducts of amines of the formula

$$R—(NR_1—(CH_2)_n—NHR_2)_x$$

where R is selected from the group consisting of aryl, alkyl, cycloalkyl, arylalkyl, alkoxyalkyl, hydroxyalkyl, and alkoxyhydroxy groups and wherein the alkyl

groups or moieties are selected from the C2-C24 alkyls, R_1 and R_2 are individually selected from the group consisting of H and C1-C4 alkyls, n is from about 2-12, and x is from about 1-8

21. The method of claim 17, said adduct being an adduct of a fatty acid amine and an acid.

22. The method of claim 21, said fatty acid amine being a C8-C24 fatty acid amine.

23. The method of claim 22, said fatty acid amine being coco-1,3-diaminopropane.

24. The method of claim 21, said acid comprising benzoic acid.

25. The method of claim 17, said composition being in the form of an aqueous dispersion.

26. The method of claim 25, said aqueous dispersion comprising from about 1-1.5 lbs. of said composition per gallon of aqueous liquid.

27. The method of claim 17, said composition being contacted with said liquid hydrocarbon at a level of from about 100-50,000 ppm of the adduct per ppm of total sulfur in the liquid hydrocarbon.

28. The method of claim 27, said level being from about 250-10,000 ppm.

29. The method of claim 28, said level being from about 300-2,000 ppm.

* * * * *