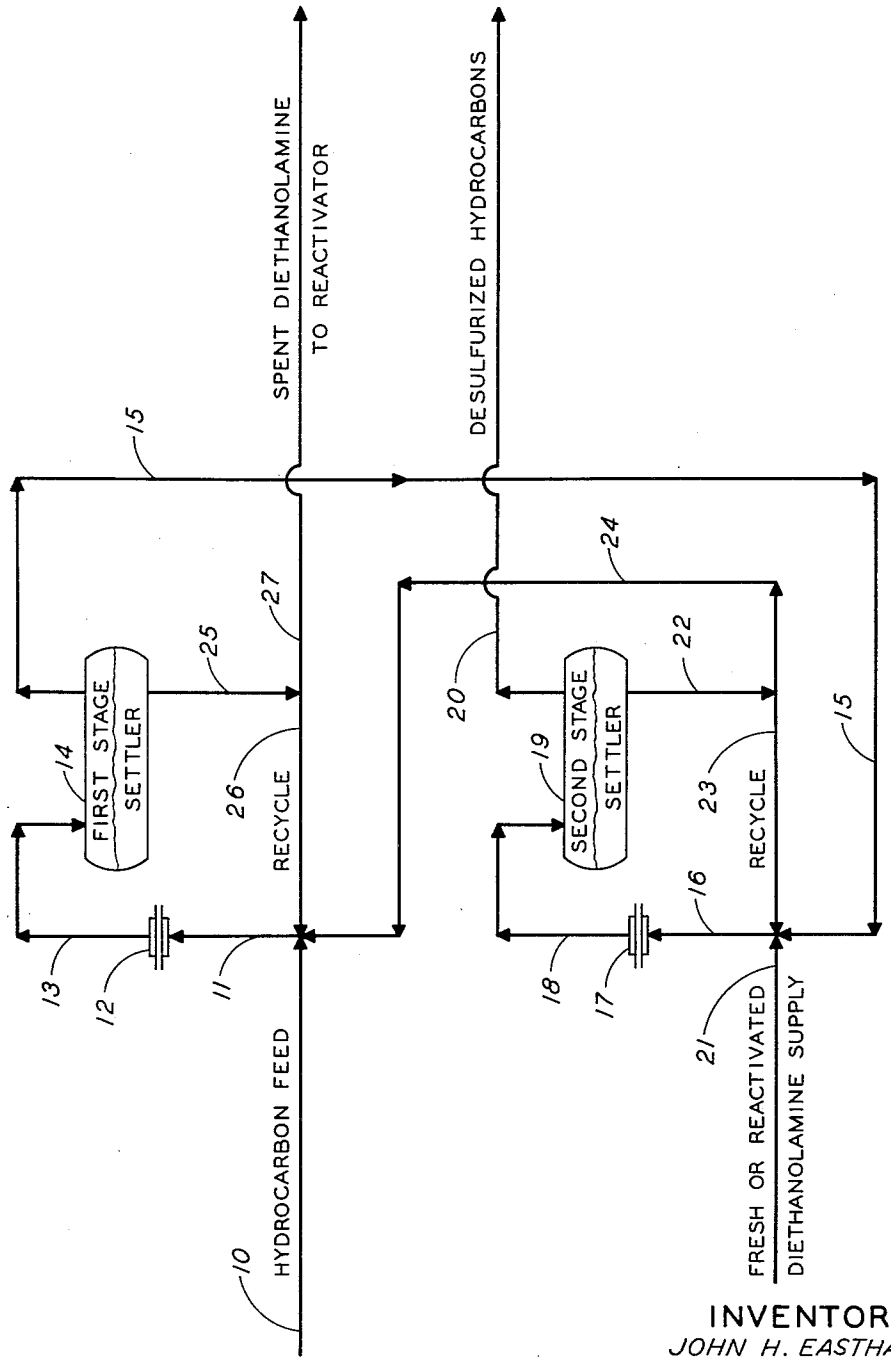
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PROCESS FOR REMOVING CARBONYL SULFIDE FORM LIQUEFIED PETROLEUM GASES

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PROCESS FOR REMOVING CARBONYL SULFIDE FROM LIQUEFIED PETROLEUM GASES

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This invention relates to a process for removing carbonyl sulfide from liquefied petroleum gases. More particularly, it relates to the removal of carbonyl sulfide, or both carbonyl sulfide and hydrogen sulfide, from normally gaseous petroleum fractions by contacting said fractions in the liquid state with an aqueous solution of diethanolamine.

Presently there is a great demand for liquefied petroleum gases for use as household and automotive fuels. An important source of basic material for liquefied petroleum gas are C_3 and C_4 hydrocarbons produced in the various refining and cracking processes to which crude oil is subjected. The petroleum gases obtained from these processes contain appreciable quantities of sulfur-containing compounds which must be removed in order to produce a commercially acceptable liquefied petroleum gas. The usual object of the various desulfurization processes that have been developed by the industry is to reduce the sulfur content of the finished product below the point at which serious corrosion would be observed. In the case of liquefied petroleum gas, the maximum allowable sulfur content is ordinarily much lower than in other petroleum products, since even a very low sulfur content, particularly in the form of free sulfur or hydrogen sulfide, is found to cause the formation of sulfur or sulfide deposits which cause faulty operation of the equipment in which the gas is employed. Such troublesome deposits are most commonly formed in the orifices of gas-air mixing equipment in industrial and household gas systems and in carbureting units of automotive equipment. Slow accumulation of such deposits resulting in operational failure may occur even where the sulfur content of the gas is very low. Consequently, highly efficient desulfurization is sought in the production of commercial liquefied petroleum gas.

Among the sulfur-containing compounds commonly found in petroleum gases is carbonyl sulfide. This compound is rarely present in virgin petroleum fractions but is formed in most thermal and catalytic cracking operations, which are substantial sources of commercial liquefied petroleum gases. While the amount of carbonyl sulfide contained in liquefied petroleum gases derived from these cracking operations is generally small, usually on the order of several hundred parts per million, nevertheless this amount is still well beyond the allowable limits of a marketable product.

Carbonyl sulfide is relatively inactive and has the general characteristics of an acid anhydride. It is not particularly corrosive itself and its corresponding acid, monothiocarbonic acid, is not known in the free state; however, reaction of carbonyl sulfide with water results in the slow formation of hydrogen sulfide, which is corrosive, and carbon dioxide. If a liquid petroleum gas containing carbonyl sulfide is tested immediately after conventional desulfurization treatment, the treated gas will show no indication of the presence of corrosive sulfur, but upon several days' standing, if moisture is present, the presence of corrosive sulfur, as free sulfur or hydrogen sulfide, will positively show upon testing. The relatively unreactive character of carbonyl sulfide itself and the slowness of its hydrolysis to the more reactive hydrogen sulfide makes efficient carbonyl sulfide removal by conventional desulfurization methods virtually impossible.

Many methods and reagents have been proposed for the purpose of removing carbonyl sulfide and hydrogen sulfide, usually involving contact of the sulfide-containing hydrocarbons with a generally alkaline compound. Strongly alkaline solutions or suspensions of weakly basic or amphoteric metallic hydroxides, the metals of which form insoluble sulfides, have been proposed. Also, various primary amines have been employed. Kerns et al., in U. S. Patent 2,311,342, describe a process for the removal of carbonyl sulfide from hydrocarbons liquids by contacting the liquids with monoethanolamine. Reed, in U. S. Patent 2,383,416, discloses a method of removing hydrogen sulfide from hydrocarbons with an aqueous solution of diethanolamine. The Kerns and Reed patents, point out the difficulty of removing carbonyl sulfide from hydrocarbons containing it and indicate that carbonyl sulfide cannot be removed by contact with diethanolamine, Reed stating that:

"Repeated tests, over long periods of time, have shown that diethanolamine in aqueous solution is inert toward carbonyl sulphide and that there is no appreciable reaction with carbon bisulphide or aldehydes." (P. 2, 2nd col., lines 31–35.)

In the past, carbonyl sulfide and hydrogen sulfide impurities in hydrocarbon mixtures have been removed by separate processes. For example, hydrogen sulfide has been removed by employing the method of Bottoms, in U. S. Reissue Patent 18,958, in which vaporized hydrocarbon mixtures are contacted with liquid solutions of amines, after which the carbonyl sulfide is separately removed for example, with monoethanolamine, or with an aqueous solution of monoethanolamine and an alkali metal hydroxide as shown in U. S. Patent 2,594,311.

It appears that when monoethanolamine is employed to remove carbonyl sulfide from carbonyl sulfide-contaminated gases, a stable reaction product of the monoethanolamine and carbonyl sulfide is formed and the monoethanolamine cannot be regenerated for use by a simple heat treatment.

It is an object of the present invention to provide a method for effecting substantially complete removal of carbonyl sulfide from petroleum products of the type employed as liquefied petroleum gases.

It is a further object to provide a method for the removal of both carbonyl sulfide and hydrogen sulfide impurities from petroleum mixtures simultaneously.

It has been found that carbonyl sulfide can be effectively removed from normally gaseous carbonyl sulfide-containing petroleum fractions by first liquefying the hydrocarbons and then contacting them with an aqueous solution of diethanolamine. It has also been found that hydrogen sulfide can also be removed from the hydrocarbons by the same treatment and that its removal can be accomplished simultaneously with the carbonyl sulfide removal.

It has also been found that the aqueous diethanolamine solution can be regenerated for reuse by heat by dispelling all of the sulfur-containing compounds removed by the diethanolamine solution from the hydrocarbons in the contacting stage or stages.

Pursuant to the present invention, normally gaseous petroleum hydrocarbons containing carbonyl sulfide are passed in the liquid phase into a contacting zone and intimately contacted with an aqueous solution of diethanolamine. The resulting reaction mixture is then separated into two phases; one, a hydrocarbon phase having a lesser concentration of carbonyl sulfide than the original hydro-

carbon feed, and an aqueous diethanolamine phase. The aqueous diethanolamine phase can be reactivated by heat and continuously recycled to remove more carbonyl sulfide.

In a preferred embodiment of the process of the invention a plurality of serially connected contacting zones are employed, the liquefied carbonyl sulfide-containing hydrocarbon feed is passed into the first of the contacting zones and the liquefied hydrocarbons, substantially free of carbonyl sulfide, is withdrawn from the last of the contacting zones. An aqueous solution of diethanolamine is introduced into the last of the contacting zones and is withdrawn from the first contacting zone in a spent or partially spent condition, and is then passed to a reactivator where the solution is regenerated by heat and recycled to the last of the contacting zones, thereby creating a cyclic passage of diethanolamine solution. In each contacting zone, the liquefied hydrocarbon and the aqueous diethanolamine solution are intimately contacted and settled to separate a hydrocarbon phase and an aqueous diethanolamine phase. Over 99 percent of both carbonyl sulfide and hydrogen sulfide present in the original hydrocarbon feed can be removed in this manner.

A great advantage of the use of aqueous diethanolamine solution to remove both carbonyl sulfide and hydrogen sulfide from normally gaseous hydrocarbons is that the spent, or partially spent, diethanolamine solution may be reactivated, or regenerated, for further use in the contacting stages. All of the sulfur-containing compounds removed from the hydrocarbon feed by the diethanolamine can be expelled from the latter by heating and stripping with steam.

The results obtained in the employment of diethanolamine pursuant to the present invention are unexpected in two significant particulars; first, it is unexpected in view of the teachings of the prior art that any means could be found to effect carbonyl sulfide removal with diethanolamine and second, it is unexpected that diethanolamine, which has been employed in the process until its capacity to remove carbonyl sulfide is spent, can be regenerated by simple steam stripping, especially in view of the fact that carbonyl sulfide and monoethanolamine form a stable reaction product as shown in Kerns et al., U. S. Patent 2,311,342.

The appended drawing is a diagrammatic illustration of one arrangement of apparatus and process flow suitable for the practice of the invention.

To start the process, an aqueous solution of diethanolamine is introduced into the first stage settler **14** and the second stage settler **19** until both settlers **14** and **19** are approximately half full. This may be done by any convenient method, for example, the diethanolamine may be passed from the diethanolamine supply through lines **21**, **16** and **18** into the second stage settler **19**. The first stage settler **14** may be charged with diethanolamine by lines **21** and **15**.

After both settlers **14** and **19** are about half full, liquefied hydrocarbon gases containing carbonyl sulfide and hydrogen sulfide are passed as feed through lines **10** and **11**, line mixer **12**, and line **13** into the first stage settler **14**. Lines **11** and **13**, and mixer **12** constitute the first stage contacting zone. In the first stage settler **14**, two separate phase are formed. An upper layer of hydrocarbons, containing a lesser concentration of carbonyl sulfide and hydrogen sulfide than in the original hydrocarbon feed, and a lower layer of aqueous diethanolamine containing reacted carbonyl sulfide and hydrogen sulfide. The upper hydrocarbon layer is removed from the first stage settler **14** and passed through lines **15**, **16**, line mixer **17**, and line **18** into the second stage settler **19**. Lines **16** and **18**, and mixer **17** constitute the second stage contacting zone. The hydrocarbon may be taken directly from line **15** as a product but in preferred operation it passes into the second stage settler as described. Two phases again separate in the second stage settler **19**; an upper hydrocarbon layer and an aqueous diethanolamine lower layer. The purified hydrocarbon product substantially free of both carbonyl sulfide and hydrogen sulfide is removed from the second stage settler **19** by line **20** and is then sent to storage or sales facilities.

At the same time as the hydrocarbon feed is treated as described above, a fresh or reactivated aqueous solution of diethanolamine is passed from the diethanolamine supply through lines **21** and **16**, line mixer **17**, and line **18** into the second stage settler **19**. In the second stage contacting zone, i. e. lines **16** and **18** and mixer **17**, the diethanolamine solution is thoroughly mixed with the hydrocarbon mixture which is passing from the first stage settler **14** to the second stage settler **19**. The diethanolamine solution in settler **19** settles forming a lower layer which is removed by line **22**, the rate of removal being adjusted to keep the second stage settler **19** about half full of said lower diethanolamine layer. A portion of the lower layer removed from settler **19** by line **22** may be re-introduced into line **16** by line **23** as recycle. The remainder of the lower layer removed by line **22** is passed through lines **24**, **11** and **13** into the first stage settler **14**. In the first stage contacting zone, i. e. lines **11** and **13**, and mixer **12**, the partially spent diethanolamine solution is thoroughly mixed with the fresh hydrocarbon feed. The diethanolamine lower layer formed in settler **14**, except for that required to keep the first stage settler **14** partially full of said lower layer, is passed through line **25**, and a portion of the diethanolamine may be recycled to line **11** by line **26**, and the remainder passes through line **27** to storage or reactivation facilities.

It is readily apparent from the foregoing description that various modifications of the process can be made within the spirit of the present invention and the scope of the appended claims. For example, the process is suitable for use in conjunction with processes that remove only hydrogen sulfide, thereby utilizing the present invention only for carbonyl sulfide removal. A still further modification is the passing of the diethanolamine effluent from line **27** which is only partially spent into a vapor phase process which utilizes diethanolamine as an agent for the removal of hydrogen sulfide. Further, many equipment or apparatus modifications may be made by those skilled in the art, and still not depart from the scope of the present invention.

The following examples illustrate the removal of carbonyl sulfide and hydrogen sulfide from normally gaseous hydrocarbons pursuant to the invention.

Example I

A gaseous hydrocarbon feed composed of 95.0% (by volume) C_3 hydrocarbons, 4.75% hydrogen sulfide, and 0.25% carbonyl sulfide was passed in the vapor phase into a contacting zone, where it was intimately contacted with a reactivated aqueous diethanolamine solution of the concentration 18% (by weight) diethanolamine. The hydrocarbon feed treated in one operating day contained 22,800 pounds of hydrogen sulfide and 1,320 pounds of carbonyl sulfide. The hydrocarbons were removed from the contacting zone and the weight of both hydrogen sulfide and carbonyl sulfide was determined. The effluent from the contacting zone contained 135 pounds per day of hydrogen sulfide, and 750 pounds per day of carbonyl sulfide. Thus, vapor phase contact of the hydrocarbon feed with aqueous diethanolamine solution removed 99.0% of the hydrogen sulfide present in the feed, and only 43.1% of the carbonyl sulfide.

Example II

A hydrocarbon feed similar to that of Example I was treated pursuant to the invention and contained the fol-

lowing sulfur compounds in the proportions and amounts shown:

	Weight Percent	Pounds Per Day
Hydrogen Sulfide	3.85	2,930
Carbonyl Sulfide	.58	445
Mercaptans	.37	280

The liquefied feed was passed at a rate of 430 barrels per day and a pressure of 260 p. s. i. g. into the first stage settler and contacted with an 18% (weight percent) reactivated aqueous solution of diethanolamine, circulated through the first stage contacting zone at the rate of 994 barrels per day. The volume ratio of diethanolamine solution to feed treated is thus 2.31/1.0. Inspections on the treated product are tabulated below.

Compound	Weight Percent	Pounds Per Day	Percent Removal From Feed
Hydrogen Sulfide	.25	190	93.5
Carbonyl Sulfide	.006	5	98.9
Mercaptans	.33	250	10.7

The hydrocarbon effluent from the first stage settler was then introduced into the second stage settler at a rate of 430 barrels per day and a pressure of 285 p. s. i. g. and contacted with an aqueous solution of diethanolamine containing 18% (by weight) of diethanolamine circulated through the second stage settler at the rate of 925 barrels per day. The volume ratio of diethanolamine solution to hydrocarbon circulated through the second stage settler ratio was 2.15/1.0. The hydrocarbon product from the second stage settler had carbonyl sulfide and hydrogen sulfide contents as indicated below. Percentage removal of these materials from the initial feed is indicated:

Compound	Weight Percent	Pounds Per Day	Percent Removal From Original Feed (Weight)
Hydrogen Sulfide	.003	2.4	99 Plus.
Carbonyl Sulfide	.001	.7	99.84.
Mercaptans	.20	151.	46.1.

Example III

Example II is repeated, except that the liquefied C_3 feed contained sulfur compounds in the following amounts:

Compound	Weight Percent	Pounds Per Day
Hydrogen Sulfide	.58	432
Carbonyl Sulfide	.39	288
Mercaptans	.59	435

The liquefied feed was passed at a rate of 414 barrels per day and a pressure of 260 p. s. i. g. into the first stage settler and contacted with an 17.8% (weight percent) aqueous solution of diethanolamine circulating at a rate of 1030 barrels per day. The volume ratio of diethanolamine solution to feed was 2.49/1.0. Inspections of the product from the first stage treatment are tabulated below:

Compound	Weight Percent	Pounds Per Day	Percent Removal From Feed
Hydrogen Sulfide	.087	64	85.2
Carbonyl Sulfide	.0014	1	99.6
Mercaptans	.345	256	41.2

The product from the first stage settler was contacted with diethanolamine solution at the same volume as in the first stage. The final product was analyzed as in Example II (inspections are shown below):

Compound	Weight Percent	Pounds Per Day	Percent Removal From Original Feed (Weight)
Hydrogen Sulfide	.0058	4.3	99
Carbonyl Sulfide	.00014	.1	99.97
Mercaptans	.286	212	51.3

Contrasting Example I with Examples II and III, it will be noted that when the same hydrocarbon feed is contacted in vapor phase with an aqueous solution of diethanolamine, over 99 percent of the hydrogen sulfide is removed, but only 43.1 percent of the carbonyl sulfide is removed. However, if the hydrocarbon feed in liquid phase is contacted with an aqueous solution of diethanolamine, and if only one such contacting stage is employed, about 99 percent of the carbonyl sulfide is removed. However, if only one liquid contact stage is employed, only 85 to 94 percent of the hydrogen sulfide present in the original feed is removed.

Both hydrogen sulfide and carbonyl sulfide contents of the hydrocarbon feed can be reduced below 1% of their original concentration either, (1) by a first stage contact of the feed in vapor phase with aqueous diethanolamine followed by one or more stages in which the first stage product is liquefied and contacted with aqueous diethanolamine or, (2) by two or more stages in each of which the hydrocarbon feed is contacted in liquid phase with aqueous diethanolamine.

In the process of the present invention as shown in Examples II and III, volume ratios of approximately 2.5 volumes of aqueous diethanolamine solution to 1 volume of hydrocarbon feed were employed. Volume ratios of 0.1 to 1.0 up to over 5.0 to 1.0 have been used to effect over 99% carbonyl sulfide and hydrogen sulfide removal from hydrocarbon mixtures. The preferred volume ratio according to the present invention lies in the range 0.5/1.0 to 5.0/1.0 of diethanolamine solution to hydrocarbon feed.

The period of time in which the liquid hydrocarbon feed is contacted with the diethanolamine solution has varied in operation from 1 second to many minutes, but the preferred range is from 1 to 20 seconds, since any greater contact time is unnecessary to effect the over 99% removal of both carbonyl sulfide and hydrogen sulfide as is done in the present invention.

Examples II and III show an aqueous diethanolamine solution composed of 17.8 to 18.0% by weight of diethanolamine. However, diethanolamine concentrations from about 10 to about 30% have been employed to effect the same removal as accomplished in the examples, i. e. 99%, but a preferred concentration has been found to be in the range 15 to 25.

We claim:

1. The method of removing carbonyl sulfide from normally gaseous petroleum hydrocarbons containing carbonyl sulfide which comprises intimately contacting said hydrocarbon gases in liquid phase with a solution consisting of diethanolamine and water.

2. The method as defined in claim 1 wherein the volume ratio of diethanolamine solution to hydrocarbon is in the range 0.5/1 to 51.

3. The method as defined in claim 1 wherein the time of contact between the hydrocarbon and the diethanolamine solution is in the range 1 to 20 seconds.

4. The method as defined in claim 1 wherein the concentration of aqueous diethanolamine solution is in the range from about 10 to 30% by weight of diethanolamine.

5. The process of removing carbonyl sulfide from carbonyl sulfide-containing normally gaseous hydrocarbons

which comprises passing said hydrocarbons in liquid phase into a contacting zone and intimately contacting said hydrocarbons with a solution consisting of diethanolamine and water, separating the mixture into a hydrocarbon phase having a lesser concentration of carbonyl sulfide than said hydrocarbon feed, and an aqueous diethanolamine phase, heating said separated diethanolamine phase and passing steam through it to strip the absorbed carbonyl sulfide therefrom and regenerate said diethanolamine phase, cooling said phase and contacting further quantities of carbonyl sulfide-containing liquefied hydrocarbons with the regenerated diethanolamine phase.

6. The process for removing carbonyl sulfide from carbonyl sulfide-containing normally gaseous hydrocarbon feed which comprises passing said hydrocarbons in liquid phase into a contacting zone and intimately contacting said hydrocarbons in liquid phase with a solution consisting of diethanolamine and water, separating the mixture into a hydrocarbon phase having a lesser concentration of carbonyl sulfide than said hydrocarbon feed, and an aqueous diethanolamine phase, passing said liquid hydrocarbon phase into a second contacting zone and intimately contacting it with an aqueous solution of diethanolamine, separating the mixture into a liquid hydrocarbon phase substantially free of carbonyl sulfide, and an aqueous diethanolamine phase.

7. The process for removing carbonyl sulfide from carbonyl sulfide-containing normally gaseous hydrocarbon feed which comprises passing said hydrocarbon feed in liquid phase into a contacting zone and contacting said hydrocarbon feed in liquid phase with an aqueous solution of diethanolamine, separating the mixture into a hydrocarbon phase having a lesser concentration of carbonyl sulfide than said hydrocarbon feed, and an aqueous diethanolamine phase, passing said liquid hydrocarbon into a second contacting zone and intimately contacting it with an aqueous solution of diethanolamine, separating the mixture into a liquid hydrocarbon phase substantially free of carbonyl sulfide, and an aqueous diethanolamine phase, and passing the separated aqueous diethanolamine phase from the second contacting zone into the first contacting zone.

8. The process for separating carbonyl sulfide from carbonyl sulfide-containing normally gaseous hydrocarbon which comprises maintaining a plurality of serially connected contacting zones, liquefying the normally gaseous hydrocarbon feed and passing it into the first of the serially connected contacting zones and withdrawing liquefied hydrocarbons substantially free of carbonyl sulfide from the last of said contacting zones, passing an aqueous solution of diethanolamine into the last of said contacting zones and withdrawing spent diethanolamine solution from the first of said contacting zones, and in each zone intimately contacting the liquefied hydrocarbon and aqueous diethanolamine solution and settling the resultant mixture to separate a hydrocarbon phase and an aqueous diethanolamine phase.

9. The process for separating carbonyl sulfide from carbonyl sulfide-containing normally gaseous hydrocarbon which comprises maintaining a plurality of serially connected contacting zones, liquefying the normally gaseous hydrocarbon feed and passing it into the first of the serially connected contacting zones and withdrawing liquefied hydrocarbons substantially free of carbonyl sulfide from the last of said contacting zones, passing an aqueous solution of diethanolamine into the last of said contacting zones and withdrawing spent diethanolamine solution from the first of said contacting zones, heating said spent diethanolamine solution and passing steam through it to strip the absorbed carbonyl sulfide therefrom and regenerate said solution, cooling said solution and passing said regenerated diethanolamine solution into the last of said contacting zones, and in each zone intimately contacting the liquefied hydrocarbon and aqueous diethanolamine solution and settling the resultant mixture to separate a hydrocarbon phase and an aqueous diethanolamine phase.

10. The process for removing carbonyl sulfide from carbonyl sulfide-containing normally gaseous hydrocarbon feed which comprises passing said hydrocarbons in liquid phase into the first of two contacting zones and intimately contacting said hydrocarbons in liquid phase with a partially spent aqueous diethanolamine solution effluent from the second contacting zone, separating the mixture into a hydrocarbon phase having a lesser concentration of carbonyl sulfide than said hydrocarbon feed and an aqueous phase of spent diethanolamine, withdrawing the spent diethanolamine phase from the first contacting zone and passing the said liquid hydrocarbon phase into the second contacting zone and intimately contacting it with a fresh aqueous solution of diethanolamine, separating the mixture into a liquid hydrocarbon phase substantially free of carbonyl sulfide, and an aqueous phase of partially spent diethanolamine solution, withdrawing the hydrocarbon phase as a product, withdrawing the partially spent aqueous diethanolamine solution from the second contacting zone and passing it into the first contacting zone.

11. The process for removing carbonyl sulfide and hydrogen sulfide from a normally gaseous hydrocarbon feed containing substantial amounts of these materials which comprises passing the carbonyl sulfide and hydrogen sulfide-containing hydrocarbons into a contacting zone and intimately contacting said hydrocarbons in vapor phase with an aqueous solution of diethanolamine, removing the gaseous hydrocarbons from said contacting zone, liquefying the normally gaseous hydrocarbon effluent from the contacting zone, passing the said liquefied hydrocarbons into a second contacting zone and intimately contacting said liquid hydrocarbons with an aqueous solution of diethanolamine, separating the mixture into a liquid hydrocarbon phase having a lesser concentration of carbonyl sulfide and hydrogen sulfide than said hydrocarbon feed, and an aqueous diethanolamine phase, passing the separated diethanolamine phase from the second contacting zone into the first contacting zone, passing said liquid hydrocarbon phase into a third contacting zone and intimately contacting it with an aqueous solution of diethanolamine, separating the mixture into a liquid hydrocarbon phase substantially free of carbonyl sulfide and hydrogen sulfide, and an aqueous diethanolamine phase, and passing the separated diethanolamine phase from the third contacting zone into the second contacting zone.

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