

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Removal of Acidic Gases from Gaseous Mixtures

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the removal of acidic gases from gaseous mixtures by means of a selective absorbent.

In the present specification the term "gas" stands for both gas and vapour.

A number of methods have previously been proposed for the purification of gases contaminated with acidic components such as hydrogen sulphide and carbon dioxide. Some of these methods employ aqueous solutions of alkanolamines and involve the formation of alkanolamine salts of the acid gases, these salts being subsequently decomposed, usually by heating, to regenerate the solution and to drive off the absorbed compounds. Such solutions, however, have only a relatively limited solubility for acid gases even when the latter are under a high partial pressure, which results in the necessity to use high solution-to-gas ratios.

As distinct from such "chemical solvents", certain classes of materials are regarded as "physical solvents". Examples thereof are N-alkylated pyrrolidones and N-alkylated piperidones, which appear to act in a purely physical manner, absorbing acidic gases physically without the formation of any apparent reaction product. One of the problems encountered with such physical solvents is the difficulty of obtaining a complete or substantially complete removal of the acidic contaminants.

The present invention enables disadvantages inherent in the use of previously known absorbents to be overcome.

According to the invention, a process for the removal of acidic gases from gaseous mixtures comprises treating the gaseous mixture with a liquid absorbent which comprises at least one amine having a pK_b at 25°C of 3 to 14 and at least one member of the group consisting of N-alkylated pyrrolidones and N-alkylated piperidones, so as to obtain a liquid absorbent containing absorbed acidic gases and a gaseous stream with a reduced content of acidic gases.

For the purpose of the present specification the neutral compound carbonyl sulphide (COS) is also classified as an acidic gas, because in the process of the present invention this compound, too, is at least partly removed from the gaseous mixture that is being treated with the liquid absorbent.

The liquid absorbent comprises at least one weakly basic amine which acts as a chemical solvent, and which has a pK_b at 25°C of 3 to 14. The symbol pK_b stands for the negative logarithm of the basic dissociation constant of the amine, a strong base having a low pK_b and a weak base a high pK_b . A suitable group of amines is constituted by the alkanolamines, especially those having 1 to 4 and preferably 2 or 3 carbon atoms per alkanol radical, while especially dialkanolamines can be used with advantage, always provided that the pK_b value is within the range specified. Typical species are, inter alia, monoethanolamine, diethanolamine, dipropanolamines and mixtures thereof. Diisopropanolamine is particularly preferred. Other groups of amines which can be used are alkyl amines, phenyl alkyl amines, alkoxy alkyl amines and alkoxy aryl amines, having a pK_b value at 25°C. of

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3 to 14. Typical examples of these groups are, dimethylamine, methyl ethyl amine, phenyl ethyl amine, 2,4-phenylene diamine and methoxy ethyl diamine.

5 The liquid absorbent also comprises at least one member of the group consisting of N-alkylated pyrrolidones and N-alkylated piperidones, which acts as a physical solvent. The pyrrolidones and piperidones used may have
10 side-chains attached to the carbon atoms of the heterocyclic rings. If such side-chains are present they are preferably of the alkyl type, and the total number of carbon atoms per side-chain is then preferably one or two.
15 However, it is usually desirable to use unsubstituted N-alkylated pyrrolidones and piperidones. The alkyl substituent on the N atom may be any alkyl group, but preference is usually given to alkyl groups with 1 to 4
20 carbon atoms. N-methyl pyrrolidone is the most preferred physical solvent.

The amine content of the liquid absorbent is usually within the range of 7.5 to 70% wt, and preferably within the range of 30 to 60%
25 wt, the balance of the liquid absorbent consisting of one or more N-alkylated pyrrolidones and/or N-alkylated piperidones, and possibly but not necessarily other components.

30 It has been found that the presence of other components may sometimes be advantageous. Thus, liquid absorbents also containing a certain amount of water, e.g. in the range 1 to 15% wt, may sometimes be very
35 suitable, particularly because of their lower viscosity and easier and cheaper regenerability. Other components such as glycols, may also be present.

40 The most preferred liquid absorbents are mixtures of diisopropanolamine with N-methylpyrrolidone, and of diisopropanolamine with N-methyl pyrrolidone and water.

45 The liquid absorbents may be based on pure components or technical grade components; in the latter case it may sometimes be desirable or necessary to apply one or more purification treatments to the components or
their mixture before the liquid absorbent is put into use.

50 Gaseous mixtures which can advantageously be treated by the process according to the invention include natural gas, refinery gas, town gas, flue gas, and hydrogen-containing and carbon monoxide-containing gases that are
55 obtained by incomplete combustion of hydrocarbon materials or carbonaceous materials by means of air, oxygen-enriched air or oxygen, possibly in the presence of added steam. The process is particularly attractive
60 for the treatment of gaseous mixtures containing high proportions of acid gases such as hydrogen sulphide, carbon dioxide and/or carbonyl sulphide, when it is desired to obtain product gases that contain only very
65 small quantities of acidic gases. The process may be used to treat such gases which also

contain higher molecular weight hydrocarbons, suitable as gasoline components (herein termed "gasoline-type hydrocarbons"), in which case it may be adapted in such a way that a feedstock of this type is split up into acid gases, sweet gas and gasoline-type hydrocarbons.

75 The basic step in the process of the invention comprises treating the gaseous mixture with the liquid absorbent, usually at elevated pressures, e.g. in the range 7 to 70 kg/cm². Countercurrent contacting in an absorber column is usually preferred. In such an operation intimate contacting is effected in a vertical column, the treated gas leaving the column near or at the top while the "fat" liquid absorbent (containing extracted acidic gases) leaves at or near the bottom of the column. The column is preferably provided with fractionating plates, baffles or other gas-liquid contacting means. 85

It is often useful, particularly when the feed gas contains gasoline-type hydrocarbons, to conduct the absorption operation of such an absorber column under rectified absorber conditions. 90

Other known processes and equipment for the contacting of gaseous mixtures with liquid absorbent may also be used. 95

The "fat" liquid absorbent contains physically and chemically dissolved acid gases such as hydrogen sulphide, carbon dioxide and carbonyl sulphide, possibly together with gasoline-type hydrocarbons, originally present in the gaseous mixture. It is normally subjected to regeneration and then re-used in the process. 100

105 The process according to this invention is especially attractive due to the reduced amount of liquid absorbent required for the absorption of a given amount of acid gases as compared with the absorption of a similar amount of acid gas by means of aqueous alkanolamine solutions. Thus, high degrees of acidic gas removal are obtained at quite low absorbent-to-gas ratios. A further important advantage of the use of the liquid absorbent of this invention compared with aqueous alkanolamine absorbents lies in the small heat capacity of the present mixed absorbent as compared with aqueous alkanolamine solution. Consequently, even at a given volumetric flow of absorbent the process heat and cooling water requirements for an integrated absorption-regeneration system are much lower. 110 115 120

Another advantage resides in the possibility of achieving selective hydrogen sulphide removal from gaseous mixtures that contain both hydrogen sulphide and carbon dioxide, such selective removal being possible by reducing the contact time between the gaseous mixture and the liquid absorbent, e.g. by reducing the number of contacting trays or the depth of the absorption liquid on the trays. 125

A further advantage is that aqueous liquid 130

absorbent according to the invention makes it possible to handle feed gases containing large amounts of normally liquid hydrocarbons, which are much more difficult to treat with ordinary aqueous alkanolamine absorbents. This is due to the fact that if such streams were so treated, a liquid hydrocarbon phase would separate out at the bottom of the absorber column due to the very limited hydrocarbon solubility in aqueous alkanolamines.

The regeneration of the "fat" absorption liquid may be carried out in a manner known per se, e.g. by heating and/or stripping with steam. Thus, the "fat" liquid may be stripped with steam in countercurrent operation in a vertical regeneration or stripping column.

The advantages of the version of the process wherein a liquid absorbent according to the present invention that contains a low percentage of water is used, are mainly apparent in the regeneration of the "fat" liquid absorbent by means of steam. The presence of a small proportion of water (e.g. 1 to 15%) has been found to permit the use of substantially lower regeneration temperatures than are required when a water-free absorbent is used. Thus, it is possible to employ regeneration temperatures between about 110°C and about 190°C at pressures between about 1 and about 3 kg/cm² abs. when the above proportion of water is present, while for the complete regeneration of corresponding anhydrous absorbents temperatures are required which may be over 200°C even when employing rather expensive vacuum stripping. The use of these lower temperatures has several advantages. Firstly, the thermal degradation of the organic components of the liquid absorbent is greatly reduced. Secondly, the differential in temperature between the absorber column and the regeneration column is held to a minimum, thus making the heating and cooling requirements far less stringent than in an anhydrous absorbent system.

The acidic gases leave the regeneration column at or near the top and are usually cooled so as to condense the water contained therein. At least part of this water is usually recycled to the regeneration column as a reflux stream so as to ensure the desired water content of the liquid absorbent; additional water may even have to be supplied in some cases.

In view of the easier regenerability it is preferred to employ a liquid absorbent with a high water content. The proportion of water should not, on the other hand be so high that the water content of the treated gas may become undesirably high. A higher water content of the liquid absorbent furthermore reduces the absorption capacity of the liquid absorbent for acidic gases, although this disadvantage may to a certain extent be compensated by a selective reduction of the solubility of hydrocarbons. In view of this, water

contents of the liquid absorbent within the stated limits of 1 to 15% wt are usually preferred.

In those cases in which the "fat" absorption liquid contains appreciable amounts of gasoline-type hydrocarbons it may sometimes be attractive to conduct this absorbent from the bottom part of the absorber column to a flashing zone wherein the pressure is reduced (to e.g. 1.5 to 8 kg/cm² abs.) for the purpose of removing at least part of the co-absorbed hydrocarbons together with the smallest possible amount of the acid gas. In the subsequent regeneration column the remaining solution is heated to a temperature sufficient to volatilize the remaining acid gases, which leave the column at or near the top. In this column the pressure may, if desired, be somewhat lower than in the flashing zone.

In a preferred embodiment of the present invention gasoline-type hydrocarbons that are obtained in admixture with the acid gases in the flashing and/or regeneration zones are separated therefrom by contacting the acid gases with a sponge oil comprising gas oil hydrocarbons. The latter normally have from 12 to 18 carbon atoms per molecule. In this way the gasoline-type hydrocarbons are extracted from the acid gases. The acid gases are then ready for storage or further use, for instance the production of sulphur in a Claus plant. The presence of hydrocarbons in gas mixtures that are to be processed in Claus plants may be undesirable because of the possibility of producing discoloured sulphur.

The removal of gasoline-type hydrocarbons from the acid gases with a sponge oil may be effected in a top section of the flasher zone or the regeneration column or in separate scrubber towers following the flasher and/or the regeneration column, preferably at a temperature of 25 to 85°C.

The "fat" sponge oil, containing extracted gasoline-type hydrocarbons, may be regenerated, e.g. by heating it so as to evaporate the gasoline-type hydrocarbons. The volatilized gasoline-type hydrocarbons may be freed from any residual acid gas by rectification, if necessary.

The following Examples illustrate the invention.

EXAMPLE I

A refinery gas containing 8.65% vol of hydrogen sulphide, 2.52% vol of carbon dioxide, 0.0033% vol of mercaptan sulphur and 0.01% vol of sulphur in the form of carbonyl sulphide was treated according to the process of the invention with a liquid absorbent containing 45% by weight of diisopropanolamine, 40% by weight of N-methyl pyrrolidone and 15% by weight of water.

Use was made of a vertical absorption column provided with 30 bubble cap trays.

The gas was introduced near the bottom of this column at a rate of 13,400 standard cubic metres per hour (0°C, 1 atm abs.), the inlet temperature being 40°C.

- 5 The liquid absorbent was introduced near the top at a rate of 37,000 kg per hour, its temperature also being 40°C. The temperature in the bottom part of the column was about 55°C, whereas the temperature in the top part was about 40°C. The absorption was carried out at a pressure of about 20 atm. abs. The treated gas that left the absorption column at its top contained 0.0002% vol of hydrogen sulphide, 0.02% vol of carbon dioxide, less than 0.0001% vol of mercaptan sulphur and less than 0.0005% vol of sulphur in the form of carbonyl sulphide.

EXAMPLE II

- 20 A gas mixture obtained by carbon monoxide shift conversion of gasification gas and having a composition as indicated in the Table below was treated with a liquid absorbent consisting of 45% by weight of diisopropanolamine, 40% by weight of N-methyl pyrrolidone and 15% by weight of water.

- 25 The absorption was carried out in the same column as used in Example I. In this case the pressure in the column was about 25 atm. abs.

- 30 The gas mixture was introduced near the bottom of the absorption column at a rate of 20,300 standard cubic metres per hour (0°C, 1 atm. abs.) the inlet temperature being 30°C. The liquid absorbent was introduced at a rate of 205,000 kg per hour, its temperature also being 30°C. The temperature in the bottom part of the column was about 60°C, whereas its top temperature was about 31°C.

- 40 The treated gas that left the absorption column at its top had a composition as indicated in the Table below.

TABLE			
Composition of gas mixture (expressed in % vol)			
	before treatment	after treatment	
CO	3.31	4.87	
H ₂	64.16	94.26	50
CO ₂	31.86	0.02	
CH ₄	0.14	0.21	
A	0.20	0.29	
N ₂	0.15	0.23	
H ₂ O	0.18	0.12	55

WHAT WE CLAIM IS:—

1. A process for the removal of acidic gases from gaseous mixtures which comprises treating the gaseous mixture with a liquid absorbent comprising at least one amine having a pK_a at 25°C of 3 to 14 and at least one member of the group consisting of N-

alkylated pyrrolidones and N-alkylated piperidones, so as to obtain a liquid absorbent containing absorbed acidic gases and a gaseous stream with a reduced content of acidic gases.

2. A process according to Claim 1 in which the liquid absorbent also contains water.

3. A process according to Claim 2 in which the water content of the liquid absorbent is in the range 1 to 15% by weight.

4. A process according to any of the preceding claims in which the amine content of the liquid absorbent is in the range of 7.5 to 70% by weight.

5. A process according to Claim 4 in which the amine content of the liquid absorbent is in the range 30 to 60% by weight.

6. A process according to any of the preceding claims in which the amine is an alkanolamine.

7. A process according to any of the preceding claims in which the amine is diisopropanolamine.

8. A process according to any of the preceding claims in which the liquid absorbent contains an N-alkylated pyrrolidone and/or an N-alkylated piperidone which has no side-chains attached to the carbon atoms of the heterocyclic ring.

9. A process according to any of the preceding claims in which the liquid absorbent contains N-methyl-pyrrolidone.

10. A process according to any of the preceding claims in which the gaseous mixture is treated with the liquid absorbent at a pressure in the range 7 to 70 kg/cm².

11. A process according to any of the preceding claims in which the gaseous mixture to be treated also contains gasoline-type hydrocarbons.

12. A process according to any of the preceding claims in which the gaseous mixture is treated with the liquid absorbent counter-currently in an absorber column equipped with gas-liquid contacting means.

13. A process according to any of the preceding claims in which the treatment of the gaseous mixture with the liquid absorbent is conducted under rectified absorber conditions.

14. A process according to any of the preceding claims in which the "fat" absorbent is regenerated by heating and/or stripping with steam.

15. A process according to any of the preceding claims in which the "fat" absorbent is regenerated at a temperature in the range 110°C and 190°C and a pressure in the range 1 and 3 kg/cm² abs.

16. A process according to any of the preceding claims in which a gaseous mixture which contains gasoline-type hydrocarbons is treated with the liquid absorbent in an absorber column, a "fat" liquid absorbent containing gasoline-type hydrocarbons is withdrawn from the bottom of the absorber

The gas was introduced near the bottom of this column at a rate of 13,400 standard cubic metres per hour (0°C, 1 atm abs.), the inlet temperature being 40°C.

- 5 The liquid absorbent was introduced near the top at a rate of 37,000 kg per hour, its temperature also being 40°C. The temperature in the bottom part of the column was about 55°C, whereas the temperature in the top part was about 40°C. The absorption was carried out at a pressure of about 20 atm. abs. The treated gas that left the absorption column at its top contained 0.0002% vol of hydrogen sulphide, 0.02% vol of carbon dioxide, less than 0.0001% vol of mercaptan sulphur and less than 0.0005% vol of sulphur in the form of carbonyl sulphide.

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alkylated pyrrolidones and N-alkylated piperidones, so as to obtain a liquid absorbent containing absorbed acidic gases and a gaseous stream with a reduced content of acidic gases.

2. A process according to Claim 1 in which the liquid absorbent also contains water.

3. A process according to Claim 2 in which the water content of the liquid absorbent is in the range 1 to 15% by weight.

4. A process according to any of the preceding claims in which the amine content of the liquid absorbent is in the range of 7.5 to 70% by weight.

5. A process according to Claim 4 in which the amine content of the liquid absorbent is in the range 30 to 60% by weight.

6. A process according to any of the preceding claims in which the amine is an alkalamine.

7. A process according to any of the preceding claims in which the amine is diisopropanolamine.

8. A process according to any of the preceding claims in which the liquid absorbent contains an N-alkylated pyrrolidone and/or an N-alkylated piperidone which has no side-chains attached to the carbon atoms of the heterocyclic ring.

9. A process according to any of the preceding claims in which the liquid absorbent contains N-methyl-pyrrolidone.

10. A process according to any of the preceding claims in which the gaseous mixture is treated with the liquid absorbent at a pressure in the range 7 to 70 kg/cm².

11. A process according to any of the preceding claims in which the gaseous mixture to be treated also contains gasoline-type hydrocarbons.

12. A process according to any of the preceding claims in which the gaseous mixture is treated with the liquid absorbent counter-currently in an absorber column equipped with gas-liquid contacting means.

13. A process according to any of the preceding claims in which the treatment of the gaseous mixture with the liquid absorbent is conducted under rectified absorber conditions.

14. A process according to any of the preceding claims in which the "fat" absorbent is regenerated by heating and/or stripping with steam.

15. A process according to any of the preceding claims in which the "fat" absorbent is regenerated at a temperature in the range 110°C and 190°C and a pressure in the range 1 and 3 kg/cm² abs.

16. A process according to any of the preceding claims in which a gaseous mixture which contains gasoline-type hydrocarbons is treated with the liquid absorbent in an absorber column, a "fat" liquid absorbent containing gasoline-type hydrocarbons is withdrawn from the bottom of the absorber



5 column and introduced into a flashing zone wherein the pressure is reduced for removing at least part of the co-absorbed hydrocarbons together with a minimum amount of the acid gas, and the remaining solution is introduced into a regeneration column wherein it is heated to a temperature sufficient to volatilize the remaining acid gas.

10 17. A process according to any of the preceding claims in which a mixture of gasoline-type hydrocarbons and acid gas is removed from the "fat" liquid absorbent, and the gasoline-type hydrocarbons are separated from the mixture by contacting it with a sponge
15 oil comprising gas oil components.

18. A process according to any of the preceding claims in which the acidic gases contain hydrogen sulphide which is oxidized to sulphur.

19. A process for the removal of acidic 20 gases from gaseous mixtures substantially as described with reference to either of the Examples.

20. Gaseous mixtures which have been freed from acidic gases by a process as 25 claimed in any of the preceding claims.

21. Gasoline-type hydrocarbons which have been removed from a gaseous mixture by a process as claimed in Claim 17.

22. Acidic gases which have been removed 30 from gaseous mixtures by a process as claimed in any of Claims 1 to 19.

23. Sulphur which has been produced by a process as claimed in Claim 18.

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