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PATENT SPECIFICATION

DRAWINGS ATTACHED

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Int. Cl.:—B 01 d // C 07 c, C 10 b

COMPLETE SPECIFICATION

Purification of Gaseous Mixtures containing Hydrogen Sulphide

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 purification of gases (which term as used herein includes gaseous mixtures) contaminated with hydrogen sulphide and possibly carbon dioxide and/or carbon oxysulphide and/or water, by means of a selective absorbent.

The invention is applicable more particularly, but not exclusively, to the purification of a gaseous mixture of low molecular weight hydrocarbons (as hereinafter defined).

The term "low molecular weight hydrocarbons" as used herein means hydrocarbons having 1 to 3 carbon atoms per molecule (C_1—C_3).

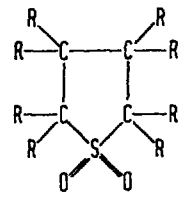
The invention is likewise applicable to the purification of hydrogen-containing gas.

A number of methods have previously been proposed for the purification of such gases.

In many instances aqueous solutions of alkanolamines are utilized, which often results in undue corrosion of processing equipment. It is often observed as well that unduly large proportions of aqueous solutions are required in order to obtain the desired degree of purity of the treated gas. This requires excessive capital expenditure in order to treat a given quantity of gas. Another disadvantage of many selective absorption processes is the necessity for a separate dehydration step, since absorbents such as aqueous alkanolamines or glycol solutions do not selectively remove water at the same time as they absorb gases such as hydrogen sulphide. Since in many instances water cannot be tolerated in the sweet gas stream the need for removing water constitutes an additional cost factor in the processing gases containing appreciable amounts of water. In many selective absorption processes it is necessary to arrange for separate treating steps and additional cumbersome equipment for the removal of gasoline hydrocarbon components (as hereinafter defined) which may be present.

The term "gasoline components" as used herein means hydrocarbons having 4 to 12 carbon atoms per molecule (C_4—C_{12}).

According to the invention, a process for the purification of a gas defined as hereinbefore contaminated with hydrogen sulphide and possibly with other contaminants such as carbon dioxide and/or carbon oxysulphide and/or water, which comprises intimately contacting the contaminated gas with a selective solvent consisting essentially of a sulphone of the general formula:



wherein at least four of the R's are hydrogen and any remaining R's are alkyl groups having from one to four carbon atoms each.

The said sulphones are based upon cyclotetramethylene sulphone, the basic and preferred species being sulpholane, otherwise referred to as thiophene tetrahydro-1,1-dioxide. Suitable derivatives of the basic compound include 2,3-dimethyl cyclotetramethylene sulphone; 2,4-dimethyl cyclotetramethylene sulphone; 2,5-dimethyl cyclotetramethylene sulphone; 3-ethyl cyclotetramethylene sulphone; and 2-methyl 5-propyl cyclotetramethylene sulphone as well as their analogues and homo-

[*Price 4s. 6d.*]

logues. It is preferred no more than 2 alkyl substituents are appended to the tetramethylene sulphone ring.

Preferably the solvent comprises a sulphone and 1—10% of hydrocarbons having from 8 to 12 carbon atoms per molecule. The principal purpose of this is to facilitate the subsequent stripping step to which the impurity-laden solvent is subjected. Since the sulphone has a relatively high boiling point, the solution must be heated to an unsuitably high temperature for substantially complete removal of acid gases therefrom. When a hydrocarbon having from 8 to 12 carbon atoms is present as a modifying component of the solvent this component boils at a substantially lower temperature than the sulphone and acts as a stripping agent, carrying with it as it volatilizes any acidic gases present in the liquid solvent phase.

The gases which may be purified in accordance with this invention include refinery and natural gases, and also hydrogen-containing gases such as are obtained in catalytic reforming processes, recycle gas for hydro-desulphurization processes and gases obtained by partial combustion of hydrocarbons with oxygen-containing gases. The process is particularly suitable for the purification of natural gases having high hydrogen sulphide contents, e.g. in the order of 10—80% by weight of hydrogen sulphide. These gases, and particularly natural gas, may contain not only substantial amounts of hydrogen sulphide together with normally gaseous hydrocarbons such as methane and ethane, but may also contain carbon dioxide in substantial quantities as well minor proportions of gasoline-range hydrocarbons such as C_4—C_7 hydrocarbons, while water vapour will practically always be present. Gaseous mixtures produced in such refining operations as thermal or catalytic cracking may contain not only the above components, but also such derivatives as carbon oxysulphide.

The basic step in the process of this invention comprises intimate contacting, preferably counter-currently, between the gas and the liquid sulphone solvent, if desired containing also C_8—C_{12} hydrocarbons (in the following defined as "modified sulphone") under a pressure preferably in excess of 7 kg/cm² absolute and up to much higher pressures such as 70—150 kg/cm² absolute. The temperature at which intimate contacting is effected is immaterial, but it is preferred to operate between 10°C and 65°C, more preferably between 26°C—49°C. Normally, intimate contacting would take place in a vertically-positioned tower equipped with baffles, trays or similar devices to improve the contacting between the gas to be purified and the solvent so that the impurities are removed progressively from the gas. The sweet gas leaves the tower near or at the top while the fat solution leaves the tower at or near the bottom. If desired, heat may be supplied as by a steam coil near the bottom of the tower, this section of the tower being heated to a temperature of 38°C—177°C. Optionally, the tower may be constructed as a rectified contacting zone to maintain a differential in temperature between the top and bottom sections of the tower.

The fat solution of hydrogen sulphide and other impurities may be cooled through a heat exchanger and passed to a gas stripper at substantially reduced pressures of, for instance, 0.15—1.75 kg/cm²abs. In the gas stripper the fat solution is heated to an elevated temperature to volatilize the absorbed gases which will leave the stripper at the top. Stripping is assisted if a relatively low boiling inert liquid is present such as hydrocarbons having from 8 to 12 carbon atoms per molecule. Under these circumstances removal of the absorbed gases can be realized at substantially lower temperatures and the rate of gas evolution is accelerated. The bottom of the stripper may be heated to a temperature in the range of 150°C—205°C by means of a reboiler.

If a C_8—C_{12} hydrocarbon fraction is used as a stripping aid it is recommended to pass the stripped gases through a cool section near the top of the gas stripper. If cooled to approximately 10°C—65°C, the vapours of the stripping hydrocarbon fraction are condensed and may be returned to the stripped solvent for recycle to the high pressure absorber. The reconstituted lean solvent is then repressured on its recycle route to the absorber.

The hydrogen sulphide, assuming it is uncontaminated with either stripping hydrocarbon fraction or other hydrocarbon components, can then be channelled to, for instance, a sulphur-producing plant such as a Claus sulphur plant wherein essentially pure hydrogen sulphide is partially oxidized to sulphur.

If the gas to be purified contains higher molecular weight hydrocarbons, these will have been extracted from the feed in the absorber. These higher molecular weight hydrocarbons can be readily removed by scrubbing the gases leaving the stripper with a "sponge oil," which may be otherwise referred to as an absorber oil. The sponge oil is preferably a gas oil or lubricating oil having a somewhat higher boiling range than the gasoline hydrocarbons which are to be extracted from the gases. The preferred type of sponge oil is one predominating in hydrocarbon components having from 12 to 18 carbon atoms per molecule. Intimate contacting, preferably counter-current, in a scrubber at temperatures of 26—65°C is preferred. The fat sponge oil, containing gasoline hydrocarbons, may be warmed by indirect heat exchange with lean sponge oil being recycled to the sponge oil scrubber. This warmed fat sponge oil may then be passed to a gasoline hydrocarbon stripper which is usually heated by means of a steam coil to a temperature of 50—205°C, at the

	Gas to be purified	Purified gas leaving top of rectified absorber	Vapours leaving top of stripper	Hydrocarbons recovered in gasoline hydrocarbon absorber
H_2S	45.3	10 ppm	88.5	200 ppm
CO_2	4.5	1.8	7.2	—
N_2	3.2	6.3	0	—
H_2O	800 ppm *a*)	50 ppm *b*)	1000 ppm	1000 ppm
C_1	40.1	85.1	1.7	—
C_2	2.7	5.1	1.0	—
C_3	0.7	1.0	1.3	1.5 ppm
C_4	0.4	0.4	0.2	2.5
C_5	0.3	0.2	0.1	3.0
C_6+	2.7	0.1	0	93

a) + 90° F. dew point

b) + 5° F. dew point

Test conditions

Synthetic feed gas:
temperature 32.2°C
pressure 77.3 kg/cm² abs.

Solvent:
sulpholane with 10% by wt. n. octane

Absorber (11):
rectified absorber with 30 trays
top temperature: about 32°C
bottom temperature: about 82°C

Solvent flow:
2 moles solvent/mole feed gas

Stripper (21):
pressure 2 kg/cm² abs.
temperature at feed inlet: about 65.6°C
temperature at top (condenser): about 32°C
reboiler temperature: about 149°C.

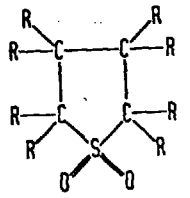
Gasoline Hydrocarbon Absorber (H_2S feed gas) (25):
temperature: about 26.5C
pressure: 2 kg/cm² abs.

Sponge oil characteristics:
aromatic content: 50%
initial boiling point: 205°C
carbon atoms per molecule: average 16

Sponge oil flow:
0.3 mole/mole feed gas

WHAT WE CLAIM IS:—

1. A process for the purification of a gas as hereinbefore defined contaminated with hydrogen sulphide and possibly with other contaminants such as carbon dioxide and/or carbon oxysulphide and/or water, which comprises intimately contacting the contaminated gas with a selective solvent consisting essentially of a sulphone of the general formula:



wherein at least four of the R's are hydrogen and any remaining R's are alkyl groups having from one to four carbon atoms each.

2. A process as claimed in Claim 1 in which the gas to be purified is a contaminated gaseous mixture of low molecular weight (as hereinbefore defined) hydrocarbons.

3. A process as claimed in Claim 1 in which the gas to be purified is a contaminated hydrogen-containing gas.

4. A process as claimed in any of Claims 1 to 3, in which the sulphone is a derivative of cyclotetramethylene sulphone with not more

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C_2	2.7	5.1	1.0	—
C_3	0.7	1.0	1.3	1.5 ppm
C_4	0.4	0.4	0.2	2.5
C_5	0.3	0.2	0.1	3.0
C_6+	2.7	0.1	0	93

a) + 90° F. dew point

b) + 5° F. dew point

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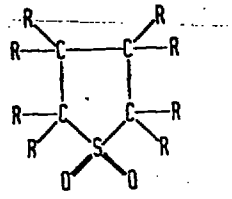

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3. A process as claimed in Claim 1 in which the gas to be purified is a contaminated hydrogen-containing gas.

4. A process as claimed in any of Claims 1 to 3, in which the sulphone is a derivative of cyclotetramethylene sulphone with not more

than two alkyl substituents having one to four carbon atoms each.

5. A process as claimed in any of Claims 1 to 3 in which the sulphone is cyclotetramethylene sulphone.

6. A process as claimed in any of Claims 1 to 5 in which the solvent comprises a sulphone and 1 to 10% by weight of hydrocarbons having from 8 to 12 carbon atoms per molecule.

7. A process as claimed in any of Claims 1 to 6 in which the intimate contacting is effected at a pressure above 7 kg/cm² absolute.

8. A process as claimed in any of Claims 1 to 7 in which the intimate contacting is effected at a temperature in the range of from 10°C to 65°C.

9. A process as claimed in any of Claims 1 to 8 in which the absorbed gases are stripped from the solvent under substantially reduced pressure.

10. A process as claimed in Claims 6 and 9 in which the stripped gases are cooled to condense C_8—C_{12} hydrocarbons originating from the solvent and the condensed hydrocarbons are subsequently recombined with the stripped solvent.

11. A process as claimed in any of Claims 1 to 10 which comprises additionally removing gasoline components as hereinbefore defined by washing the stripped gases with an absorber oil consisting essentially of C_{12}—C_{18} hydrocarbons.

12. A process as claimed in Claim 11 in which the gasoline components (as hereinbefore defined) are recovered from the absorber oil and freed from remaining hydrogen sulphide by rectification.

13. A process for the purification of a gas as hereinbefore defined, substantially as described with reference to the accompanying drawing.

14. A gas from which hydrogen sulphide and possibly other contaminents have been removed by a process as claimed in any of the preceding claims.

15. Gasoline components (as hereinbefore defined) obtained by a process as claimed in Claim 11 or Claim 12.

KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.

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