APPLICATION FOR A (8) STANDARD/PETTY PATENT

We, SNAPROGETTI S.P.A.
of Corso Venezia 16,
Milan,
Italy
hereby apply for the grant of a (8) Standard/Petty Patent for an invention entitled
"Process for the selective removal of hydrogen sulphide from gaseous mixtures also containing carbon dioxide"
which is described in the accompanying (8) complete specification.

(Note: The following applies only to Convention applications)
Details of basic application(s)

<table>
<thead>
<tr>
<th>Application No.</th>
<th>Country</th>
<th>Filing Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 740A/84</td>
<td>ITALY</td>
<td>26 November, 1984</td>
</tr>
</tbody>
</table>

Address for Service: PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia 3000

Dated @ 14 November, 1985

P. PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
SNAPROGETTI S.P.A.
AUSTRALIA

PATENTS ACT

DECLARATION FOR A PATENT APPLICATION

In support of the (a) convention application made by
SNAMPROGETTI S.P.A.

I/we (a) Mr. Carlo Cioni, c/o Snamprogetti S.p.A. of Corso Venezia 16, Milan, Italy.

We do solemnly and sincerely declare as follows:

1. I am/We are the applicant(s).
   (or, in the case of an application by a body corporate)
2. I am/We are authorized to make this declaration on behalf of the applicant(s).
   (or, where the applicant(s) is/are not the actual inventor(s))
3. Luigi Gazzi, via Muratori 32, Milan, Italy & Carlo Rescalli, via Liberta 20, Milan, Italy.

We are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

The applicant is the assignee of the invention from the actual inventor.

(Note: Paragraphs 3 and 4 apply only to Convention applications)

3. The basic application(s) for patent or similar protection on which the application is based is/are identified by country, filing date, and basic applicant(s) as follows:
   (a) Italy, 26 November, 1984, SNAMPROGETTI S.P.A. & ASSORENI

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

Declared at (a) Milan
Dated (b) 7 November, 1985

SNAMPROGETTI S.P.A.

To: The Commissioner of Patents

FITZPATRICK

PHILLIPS ORMONE & FITZPATRICK
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Melbourne, Australia
SELECTIVE REMOVAL OF H2S FROM GASEOUS MIXTURES CONTAINING CO2

SNAMPROGETTI S.p.A.

50050/85  (22) 19.11.85  (24) 26.11.84
23740/84  (32) 26.11.84  (33) IT

5.6.86

BOID 53/14  BOID 53/18

LUIGI GAZZI AND CARLO RESCALLI

PO

Claim

1. Process for the selective removal of hydrogen sulphide from gaseous mixtures also containing carbon dioxide, essentially comprising an absorption by means of a mixture of a low-boiling tertiary amine, and of an organic solvent with a water content not greater than 25% by weight, and a regeneration in a stripping column of the same absorbent solution and possibly an expansion between the absorption zone and the regeneration zone, characterized in that there are placed into contact with water in the upper absorption zone or in a zone external to it, and in the upper stripping zone, or in a zone external to it, the gaseous effluents from said zones.
AUSTRALIA

Patents Act

COMPLETE SPECIFICATION
(ORIGINAL)

Application Number: 50 050/85

Class
Int. Class

Complete Specification Lodged:

Lodged:

Accepted:

Published:

Priority

Related Art:

Name(s) of Applicant(s): SNAMPROGETTI S.p.A.

Address(es) of Applicant(s):

Corso Venezia 16,
Milan,
Italy.

Actual Inventor(s):
LUIGI GAZZI & CARLO RESCALLI

Address for Service is:

PHILLIPS, ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia, 3000

Complete Specification for the invention entitled:

"Process for the selective removal of hydrogen sulphide from gaseous mixtures also containing carbon dioxide"

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):
The present invention relates to a process for the removal of hydrogen sulphide from gaseous mixtures also containing carbon dioxide, wherein as the absorption means a mixture is used of a low-boiling tertiary amine and of an organic solvent in aqueous solution.

The use is known from the Patent in Australia No.542254 granted on 24.6.106 for the Applicant's name of mixtures of tertiary amines and of organic solvents, with a water content not greater than 10% by weight, as the absorption means.

The use of the low-boiling tertiary amines in aqueous solutions shows some drawbacks due to the fact said tertiary amines have a tendency to vapourize into the treated gas, thus rendering problematic their use.

We have found a process for the selective removal of hydrogen sulphide from hydrocarbon mixtures also containing carbon dioxide, which allows aqueous solutions of low-boiling tertiary amines to be used, without the drawback of high amine losses.

The process being the object of the present invention comprises essentially an absorption by means of a low-boiling tertiary amine, and of an organic solvent, with a water content not greater than 25% by weight, and a regeneration in a stripping column of the same absorbent solution, and possibly an expansion between the absorption zone and the regeneration zone, and is characterized in that there are placed in contact with water in the upper absorption zone or in a zone external to it, and in the upper stripping zone, or in a zone external to it, the gaseous effluents from said zones.

In case an expansion stage is provided between the ab-
sorption zone and the regeneration zone, e.g., by using a "flash tank", the gaseous effluents from the expansion zone either are sent to the lower zone of the absorption zone, or are removed from the plant, in the second case it being necessary to place said gaseous effluents in contact with water in the upper zone of the expansion zone, or in a zone external to it.

The low-boiling tertiary amines, which can be used either as single products or as mixtures thereof, according to the invention, can be selected among dimethylethanolamine, diethylethanolamine, dipropylethanolamine, diisopropylethanolamine, N-methylmorpholine.

The organic solvents, which may be used either as single products or as mixtures thereof as the components of the absorbent solution, are sulpholane, N-methylpyrrolidone, N-methyl-3-morpholone, dialkylether-monoethylene glycols, dialkylether-polyethylene glycols (wherein each alkyl group contains from 1 to 4 carbon atoms), ethylene glycol, diethylene glycol, triethylene glycol, N,N-dimethylformamide, N-formylmorpholine, N,N-dimethylimidazolidine-2-one, and N-methylimidazolc.

The contacting with water of the gaseous effluents is a stage showing characteristics and functions completely different from the water scrubbing frequently used on the purified gas coming out from the absorber's head of the not selective aminic plants. This is demonstrated by the fact that in the not selective plants, one must have the greatest care to minimize the amine content in scrubbing water, whilst it has been experimentally found in our case that the water used is always very efficacious, even when the amine concentration becomes very high. The tests have been
carried out by bubbling into water the gas deprived of \( \text{H}_2\text{S} \), but still containing \( \text{CO}_2 \). At the outlet, the content of amines (dimethylethanolamine) was constantly reduced to about 3 ppm, in contrast with the initial about 300 ppm, in spite of the high accumulation of amine in the water. The amount of \( \text{CO}_2 \) absorbed in water was stoichiometrically proportional to the amine, clearly indicating the formation of bicarbonate. All this results evident from the following Table, wherein DMEA = dimethylethanolamine.

<table>
<thead>
<tr>
<th>Progressive scrubbing time (h)</th>
<th>Moles/100 g of aqueous solution</th>
<th>Washed gas DMEA ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{CO}_2 )</td>
<td>( \text{DMEA} )</td>
</tr>
<tr>
<td>100</td>
<td>n.d.</td>
<td>0.05955</td>
</tr>
<tr>
<td>200</td>
<td>0.12500</td>
<td>0.12697</td>
</tr>
<tr>
<td>320</td>
<td>0.21591</td>
<td>0.23371</td>
</tr>
<tr>
<td>490</td>
<td>0.30000</td>
<td>0.29888</td>
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The ways of operating with water may be very different. It must be pointed out first of all, that in the plants for the selective removal of \( \text{H}_2\text{S} \), a small amount is always necessary of reintegration water, which replaces water lost by evaporation into the acidic gases, into the flash gas and into the treated gas. The raw gas is indeed usually saturated with water, but the flash gas and the acidic gases are saturated at a lower pressure; moreover, the gas treated, the flash gas and the acidic gases come out very often at a higher temperature than the raw gas; this all causes a certain water loss, to be reintegrated from the outside. The reintegration water is usually condensate water or demineralized water, in any case \( \text{H}_2\text{S} \)-free water, so that it can be certainly contacted with the treated gas.
A preferred embodiment of the present invention consists in using the reintegration water first in the upper absorption zone, or in an absorption zone external to it, then in the upper expansion zone or in a zone external to it, and finally in the upper stripping zone or in a zone external to it, taking advantage of the decrease in pressure normally existing between these three zones: this does not cause amine losses in spite of the progressive enrichment in amine of the reintegration water.

Each single operation can be carried out either in a trays-column, or in a packing-column, as well as in suitable single-stage scrubbers.

Operating with water in the stripping zone, wherein the acidic gases are removed is a slightly particular case.

As in all aminic plants, to the purpose of removing the organic components of the absorbing solution, the solvent regeneration column (stripping column) contains a short water-refluxed rectification section. This reflux however is without effect in the case of low-boiling tertiary amines.

The head condenser of the same stripping column carries out on the contrary a certain amine removal action, which may however result not complete.

It has been surprisingly found by means of experimental determinations that the removal of the amine even down to residual 3 - 5 ppm, occurs by contacting with water the gaseous effluents from the stripping zone, i.e., the acidic gases, in a condensation zone, external to the stripping zone, having a pressure drop equal to or greater than 0.2 kg/cm².

The invention is now illustrated with the aid of the
hereto attached figure, which represents a possible embodiment thereof, which is not to be considered as being a limitation of the same invention.

By means of a pipe 1 the gas to be processed is fed to the absorber 2, to which by the pipe 3 the absorbing solution is fed. Into the upper portion of the absorber re-integration water (4) is introduced, to cause the amine to react with the acidic gases. From the top of the absorber the processed gas is drawn by means of the pipe 5, from the bottom on the contrary the exhausted solution 6 is drawn, and is sent to the regeneration column 8 after having been preheated in 7.

The vapours going upwards inside the column 8 are washed in some rectification trays, at whose outlet they are constituted by acidic gases, steam and dragged amine. The steam is condensed by being admixed with a cold water stream, which it meets in countercurrent inside the packing 10. As in the packing's upper portion the temperature remains low, the amine can react with the acidic gases, and can be recovered. The acidic gases leave the plant via the pipe 11. The pump 12 circulates water, which is cooled in the heat exchanger 13. The most of water is fed to the packing 10 through the pipe 14, a small amount thereof goes back as a reflux to the rectification section below by the pipe 15.

From the bottom of the column 8 the regenerated solution 16 comes out, and is recycled by the pump 17 to the absorber 2 after having been cooled in 7, by heat exchange with the exhausted solution 6, and in 18.
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CLAIMS
The Claims defining the invention are as follows.

1. Process for the selective removal of hydrogen sulphide from gaseous mixtures also containing carbon dioxide, essentially comprising an absorption by means of a mixture of a low-boiling tertiary amine, and of an organic solvent with a water content not greater than 25% by weight, and a regeneration in a stripping column of the same absorbent solution and possibly an expansion between the absorption zone and the regeneration zone, characterized in that there are placed into contact with water in the upper absorption zone or in a zone external to it, and in the upper stripping zone, or in a zone external to it, the gaseous effluents from said zones.

2. Process according to claim 1, wherein the water used is reintegration water to compensate for the losses of water vapourized into the gaseous effluents of the plant.

3. Process according to claim 1, characterized in that there are placed into contact with water in the upper zone of the expansion zone, or in a zone external to it, the gaseous effluents from said zone.

4. Process according to claim 2, wherein the reintegration water is used first in the upper absorption zone or in the zone external to it, then in the upper stripping zone or in the zone external to it.

5. Process according to claims 1, 2 and 3, wherein the reintegration water is used first in the upper absorption zone or in the zone external to it, then in the upper expansion zone or in the zone external to it, and finally in the upper stripping zone or in the zone external to it.

6. Process according to claim 1, wherein the contact-
ing with water of the gaseous effluents of the stripping zone occurs in a condensation zone external to the stripping zone, having a pressure drop equal to or greater than 0.2 kg/cm$^2$.

7. Process according to claim 1, wherein the contacting with water of the gaseous effluents is carried out in trays-columns or packing-columns, or in suitable single-stage scrubbers.

8. Process according to claim 1, wherein the gaseous effluents from the expansion zone are sent to the lower zone of the absorption zone.

DATED: 14 November, 1985

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Attorneys for:
SNAMPROGETTI S.p.A.

[Signature]
stripping
the gaseous
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END