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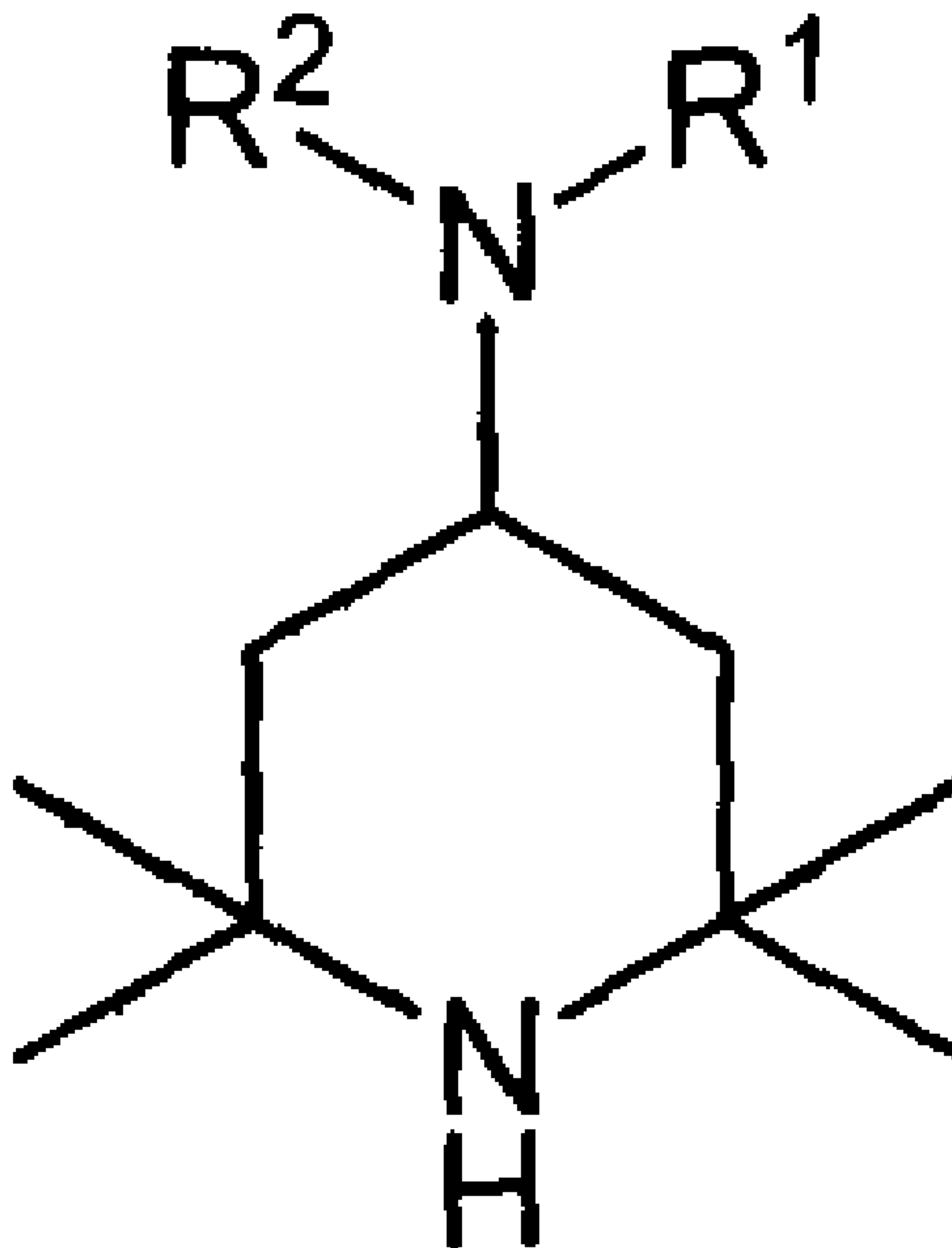
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(54) **Titre :** PROCEDE D'ABSORPTION DE CO₂ D'UN MELANGE DE GAZ

(54) **Title:** METHOD FOR ABSORBING CO₂ FROM A GAS MIXTURE



(I)

(57) **Abrégé/Abstract:**

In a method of absorbing CO₂ from a gas mixture the use of an absorption medium comprising water and at least one amine of formula (I) (see formula I), where R¹ is a -(CH₂)_n(XCH₂CH₂)_mY-R³ radical where R³ = hydrogen or an alkyl radical having from 1 to

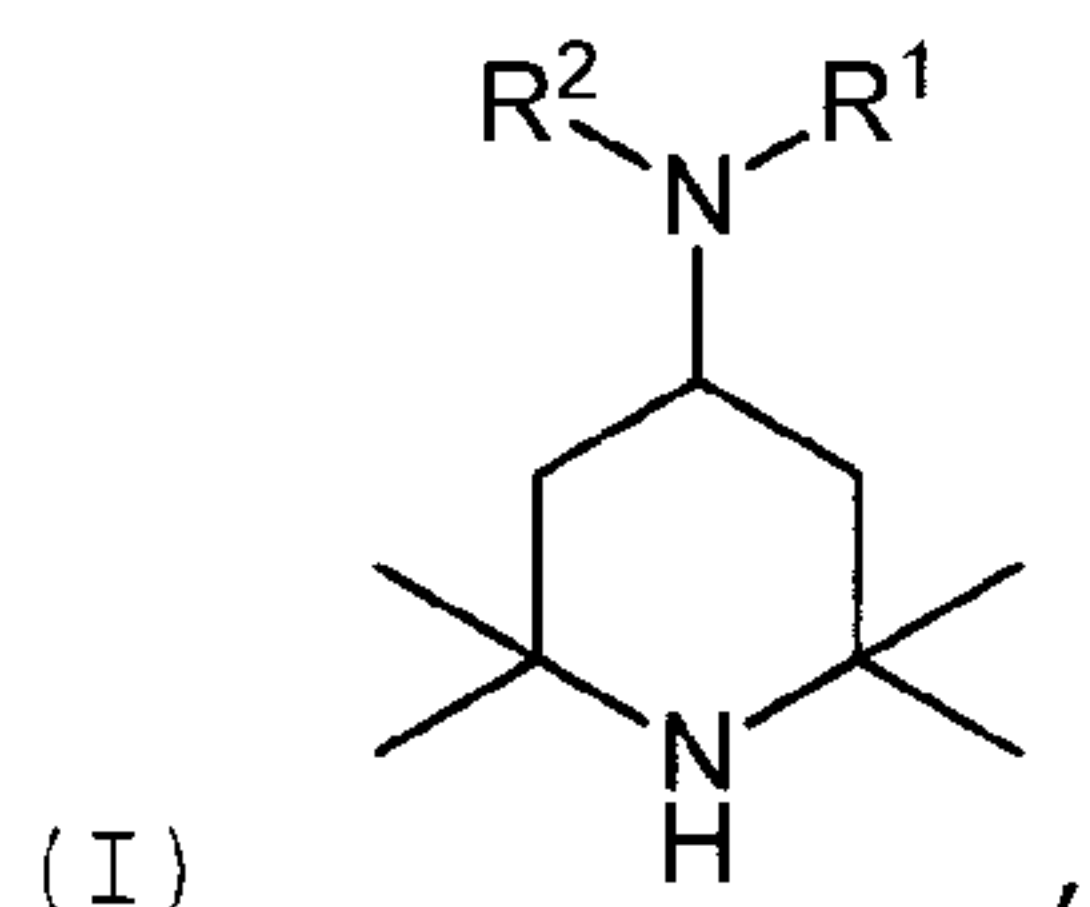
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(57) **Abrégé(suite)/Abstract(continued):**

6 carbon atoms, X and Y are each, independently of one another, NR^3 , oxygen, SO or SO_2 , where in the case of $\text{Y} = \text{SO}$ and in the case of $\text{Y} = \text{SO}_2$, R^3 is not hydrogen, and Y-R^3 can be an N-morpholinyl radical or an N-piperazyl radical, n = 2 to 4, m 0 to 4 and R^2 is hydrogen, an alkyl radical having from 1 to 6 carbon atoms or a radical R^1 , where m is not 0 when R^2 is not a radical R^1 , $\text{Y} = \text{NR}^3$ and Y-R^3 is not an N-morpholinyl radical and not an N-piperazyl radical, makes it possible to avoid precipitation of a solid during the absorption of CO_2 and a separation into two liquid phases during the regeneration of the absorption medium.

Abstract:

In a method of absorbing CO₂ from a gas mixture the use of
 an absorption medium comprising water and at least one
 5 amine of formula (I)



where

- 10 R¹ is a -(CH₂)_n-(XCH₂CH₂)_m-Y-R³ radical where
 R³ = hydrogen or an alkyl radical having from 1 to 6 carbon
 atoms,
 X and Y are each, independently of one another, NR³,
 oxygen, SO or SO₂, where in the case of Y = SO and in the
 15 case of Y = SO₂, R³ is not hydrogen, and Y-R³ can be an
 N-morpholinyl radical or an N-piperazyl radical,
 n = 2 to 4,
 m = 0 to 4 and
 R² is hydrogen, an alkyl radical having from 1 to 6 carbon
 20 atoms or a radical R¹,
 where m is not 0 when R² is not a radical R¹, Y = NR³ and
 Y-R³ is not an N-morpholinyl radical and not an N-piperazyl
 radical,
 makes it possible to avoid precipitation of a solid during
 25 the absorption of CO₂ and a separation into two liquid
 phases during the regeneration of the absorption medium.

Method for absorbing CO₂ from a gas mixture

The invention relates to a method of absorbing CO₂ from a gas mixture.

Gas streams which have an undesirable high content of CO₂ which has to be reduced for further processing, for transport or for avoiding CO₂ emissions occur in numerous industrial and chemical processes.

On the industrial scale, CO₂ is typically absorbed from a gas mixture by using aqueous solutions of alkanolamines as an absorption medium. The loaded absorption medium is regenerated by heating, depressurization to a lower pressure or stripping, and the carbon dioxide is desorbed. After the regeneration process, the absorption medium can be used again. These methods are described for example in Rolker, J.; Arlt, W.; "Abtrennung von Kohlendioxid aus Rauchgasen mittels Absorption" [Removal of carbon dioxide from flue gases by absorption] in Chemie Ingenieur Technik 2006, 78, pages 416 to 424, and also in Kohl, A. L.; Nielsen, R. B., "Gas Purification", 5th edition, Gulf Publishing, Houston 1997.

A disadvantage of these methods, however, is that the removal of CO₂ by absorption and subsequent desorption requires a relatively large amount of energy and that, on desorption, only a part of the absorbed CO₂ is desorbed again, with the consequence that, in a cycle of absorption and desorption, the capacity of the absorption medium is not sufficient.

US 7,419,646 describes a process for deacidifying off-gases in which an absorption medium is used which forms two separable phases upon absorption of the acid gas.

4-Amino-2,2,6,6-tetramethylpiperidine is cited, inter alia, in column 6 as a reactive compound for absorbing an acid gas. The process of US 7,419,646 has the disadvantage that

additional apparatus is required for separating the two phases which arise in the absorption.

US 2009/0199709 describes a similar method, in which, following absorption of the acid gas, heating of the loaded
5 absorption medium produces two separable phases which are then separated from one another. Here again, 4-amino-2,2,6,6-tetramethylpiperidine is cited as a reactive compound suitable for the absorption of an acid gas.

FR 2900841 and US 2007/0286783 describe methods for
10 deacidifying off-gases, in which the reactive compound reacted with CO₂ is separated from the loaded absorption medium by extraction. One of the reactive compounds cited for the absorption of an acid gas is 4-amino-2,2,6,6-tetramethylpiperidine.

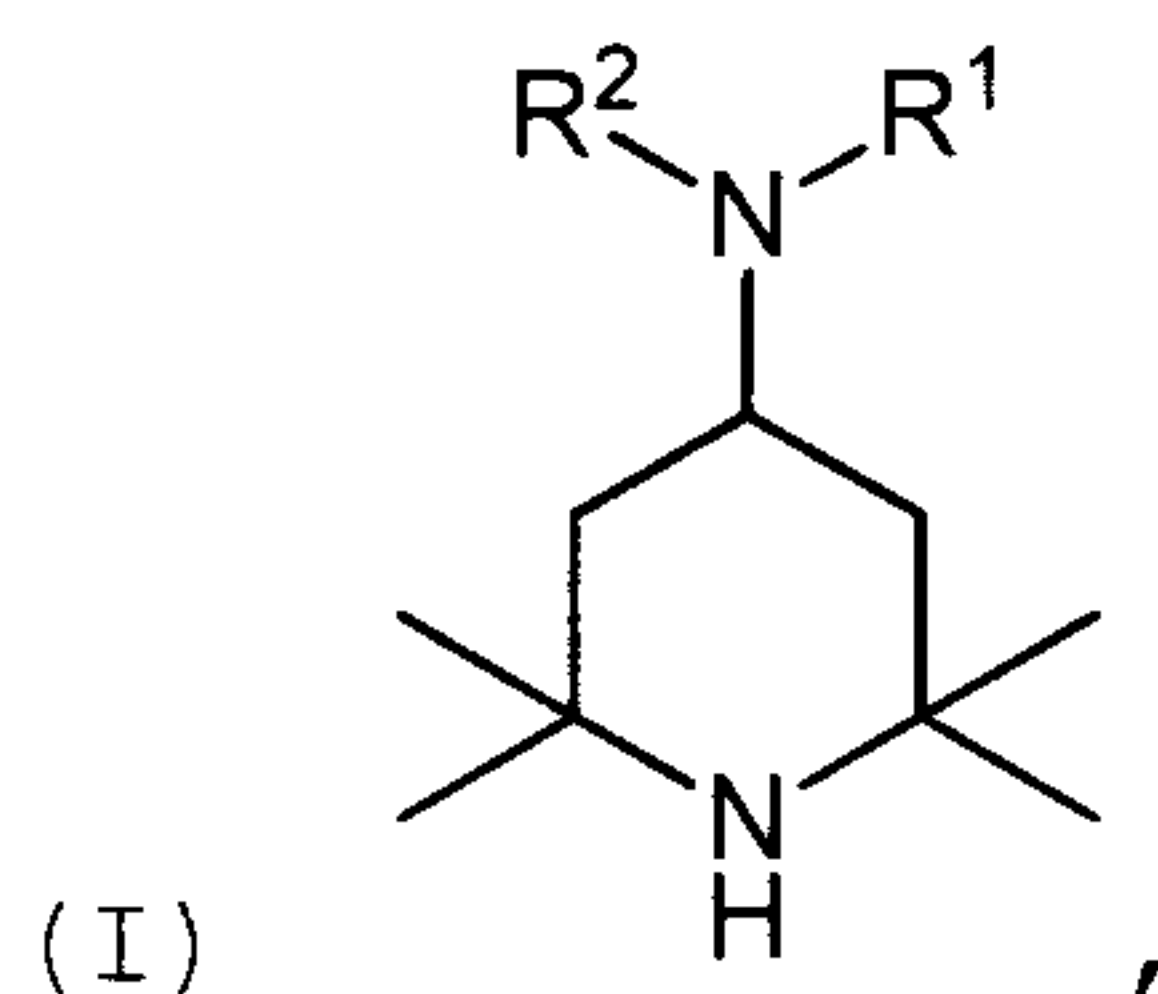
15 WO 2010/089257 describes a method of absorbing CO₂ from a gas mixture using an absorption medium that comprises water and a 4-amino-2,2,6,6-tetramethylpiperidine, which amine can be alkylated on the 4-amino group. However, precipitation of the carbamate salt readily occurs during
20 the absorption of CO₂ with absorption media comprising 4-amino-2,2,6,6-tetramethylpiperidine as the absorbant. WO 2010/089257 describes the addition of solvents, such as sulfolane or ionic liquids, in order to maintain the absorption medium single phase and to achieve a higher
25 absorption capacity for CO₂.

Therefore, there is still a need for a method of absorbing CO₂ from a gas mixture, by which at the same time a high absorption capacity for CO₂ can be achieved at a high rate of absorption and in which a separation into two liquid
30 phases or precipitation of a solid during the absorption of CO₂ and regeneration of the absorption medium can be avoided even without addition of a solvent.

It has now been found that this object can be achieved by using an absorption medium containing a 4-amino-2,2,6,6-tetramethylpiperidine substituted on the 4-amino group with the substituent on the 4-amino group carrying a
 5 suitable functional group which improves water-solubility.

The invention therefore provides a method of absorbing CO₂ from a gas mixture by bringing the gas mixture into contact with an absorption medium comprising water and at least one amine of formula (I)

10



where

R¹ is a $-(\text{CH}_2)_n-(\text{XCH}_2\text{CH}_2)_m-\text{Y}-\text{R}^3$ radical where

15 R³ = hydrogen or an alkyl radical having from 1 to 6 carbon atoms,

X and Y are each, independently of one another, NR³, oxygen, SO or SO₂, where in the case of Y = SO and in the case of Y = SO₂, R³ is not hydrogen, and Y-R³ can be an

20 N-morpholinyl radical or an N-piperazyl radical,

n = 2 to 4,

m = 0 to 4 and

R² is hydrogen, an alkyl radical having from 1 to 6 carbon atoms or a radical R¹.

25 However, m must be different from 0 when R² is not a radical R¹, Y = NR³ and Y-R³ is not an N-morpholinyl radical and not an N-piperazyl radical.

Preferably, X and Y in formula (I) are each, independently of one another, NR³ or oxygen.

30 In a particularly preferred embodiment, Y in formula (I) is oxygen, and R³ is then particularly preferably methyl or

hydrogen. Amines of formula (I) which are particularly suitable for this embodiment are

4-(2-hydroxyethylamino)-2,2,6,6-tetramethylpiperidine where $R^1 = -(\text{CH}_2)_2\text{OH}$ and $R^2 = \text{hydrogen}$,

5 4-[bis(2-hydroxyethyl)amino]-2,2,6,6-tetramethylpiperidine where $R^1, R^2 = -(\text{CH}_2)_2\text{OH}$ and $R^2 = \text{hydrogen}$,

4-(2-methoxyethylamino)-2,2,6,6-tetramethylpiperidine where $R^1 = -(\text{CH}_2)_2\text{OCH}_3$ and $R^2 = \text{methyl}$, and

10 4-(2-hydroxyethylaminoethylamino)-2,2,6,6-tetramethylpiperidine where $R^1 = -(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{OH}$ and $R^2 = \text{hydrogen}$.

In a further particularly preferred embodiment, Y-R^3 in formula (I) is an N-morpholinyl radical or an N-piperazyl radical. Amines of formula (I) which are particularly suitable for this embodiment are

15 4-(2-piperazinoethylamino)-2,2,6,6-tetramethylpiperidine where $R^1 = -(\text{CH}_2)_2\text{Y-R}^3$ and $\text{Y-R}^3 = \text{N-piperazyl}$ and

4-(2-morpholinopropylamino)-2,2,6,6-tetramethylpiperidine where $R^1 = -(\text{CH}_2)_3\text{Y-R}^3$ and $\text{Y-R}^3 = \text{N-morpholinyl}$.

20 In both particularly preferred embodiments, m in formula (I) is preferably 0.

Preferably, amines of formula (I) in which $n = 2$ or 3 , with particular preference being given to $n = 2$, are used in the process of the invention.

Amines of formula (I) can be prepared from commercial
25 triacetone amine by reductive amination, in which triacetone amine is reacted with an amine of formula $\text{R}^1\text{R}^2\text{NH}$ and hydrogen in the presence of a hydrogenation catalyst. To prepare amines of formula (I) which contain a group X or $\text{Y} = \text{SO}$ or SO_2 , the reductive amination is preferably
30 carried out using an amine $\text{R}^1\text{R}^2\text{NH}$ which has a sulphur atom in place of the group SO or SO_2 and in a subsequent step the thioether group of the resulting product is oxidized to the group SO or SO_2 by means of an oxidant. Suitable oxidants for this purpose are hydrogen peroxide, preferably

in the presence of a catalyst such as molybdate, and peroxy-carboxylic acids, preferably peroxyacetic acid.

In the method of the invention, the content of amines of formula (I) in the absorption medium is preferably from 10 to 60% by weight, particularly preferably from 20 to 50% by weight. The content is here based on the absorption medium without absorbed CO₂.

In the method of the invention, in addition to water and amines of formula (I), the absorption medium may further comprise one or more physical solvents which do not lead to any chemical reaction with CO₂. The fraction of physical solvents in this case may be up to 50% by weight. Suitable physical solvents (C) include sulfolane, aliphatic acid amides, such as N-formylmorpholine, N-acetylmorpholine, N-alkylpyrrolidones, more particularly N-methyl-2-pyrrolidone, or N-alkylpiperidones, and also diethylene glycol, triethylene glycol and polyethylene glycols and alkyl ethers thereof, more particularly diethylene glycol monobutyl ether. Preferably, however, the absorption medium of the invention contains no physical solvent.

In the method of the invention, the absorption medium may additionally comprise further additives, such as corrosion inhibitors, wetting-promoting additives and defoamers.

All compounds known to the skilled person as suitable corrosion inhibitors for the absorption of CO₂ using alkanolamines can be used as corrosion inhibitors in the method of the invention, in particular the corrosion inhibitors described in US 4,714,597. In this case, a significantly lower amount of corrosion inhibitors can be chosen than when using a customary absorption medium containing ethanolamine, since amines of formula (I) are significantly less corrosive towards metallic materials than ethanolamine.

The cationic surfactants, zwitterionic surfactants and nonionic surfactants known from WO 2010/089257 page 11, line 18 to page 13, line 7 are preferably used as wetting-promoting additive.

- 5 All compounds known to the skilled person as suitable defoamers for the absorption of CO₂ using alkanolamines can be used as defoamers in the method of the invention.

In the method of the invention, the gas mixture may be a natural gas, a methane-containing biogas from a
10 fermentation, composting or a sewage treatment plant, a combustion off-gas, an off-gas from a calcination reaction, such as the burning of lime or the production of cement, a residual gas from a blast-furnace operation for producing iron, a gas stream in a refinery, or a gas mixture
15 resulting from a chemical reaction, such as, for example, a synthesis gas containing carbon monoxide and hydrogen, or a reaction gas from a steam-reforming hydrogen production process. The gas mixture is preferably a combustion off-gas, a natural gas or a biogas.

- 20 Before being brought into contact with the absorption medium, the gas mixture preferably has a CO₂ content in the range from 0.1 to 60% by volume, particularly preferably in the range from 1 to 40% by volume.

The gas mixture can contain further acid gases from the
25 series COS, H₂S, CH₃SH or SO₂, in addition to CO₂. A combustion off-gas is preferably desulphurized beforehand, i.e. SO₂ is removed from the gas mixture by a desulphurization method known from the prior art, preferably by a gas scrub using milk of lime, before the
30 method of the invention is carried out.

For the method of the invention, all apparatus suitable for contacting a gas phase with a liquid phase can be used to contact the gas mixture with the absorption medium.

Preferably, absorption columns or gas scrubbers known from the prior art are used, for example membrane contactors, radial flow scrubbers, jet scrubbers, venturi scrubbers, rotary spray scrubbers, random packing columns, ordered
5 packing columns or tray columns. With particular preference, absorption columns are used in countercurrent flow mode.

In the method of the invention, the absorption of CO₂ is carried out preferably at a temperature of the absorption
10 medium in the range from 0 to 80°C, more preferably 20 to 60°C. When using an absorption column in countercurrent flow mode, the temperature of the absorption medium is more preferably 30 to 60°C on entry into the column, and 35 to 80°C on exit from the column.

15 The absorption of CO₂ is preferably carried out at a pressure of the gas mixture in the range from 0.5 to 90 bar, particularly preferably from 0.9 to 30 bar. The partial pressure of CO₂ in the gas mixture before absorption is preferably in the range from 0.1 to 10 bar.
20 Absorption of CO₂ from natural gas is preferably carried out at a pressure of the gas mixture in the range from 5 to 90 bar, particularly preferably from 10 to 80 bar. Absorption of CO₂ from a combustion off-gas is preferably carried out at a pressure of the gas mixture in the range
25 from 0.8 to 1.5 bar, particularly preferably from 0.9 to 1.1 bar, in order that the combustion off-gas does not have to be compressed beforehand.

In a preferred embodiment of the method of the invention, CO₂ absorbed in the absorption medium is desorbed again by
30 increasing the temperature and/or reducing the pressure and the absorption medium after this desorption of CO₂ is used again for absorbing CO₂. By such cyclic operation of absorption and desorption, CO₂ can be entirely or partially separated from the gas mixture and obtained separately from
35 other components of the gas mixture.

As an alternative to the increase in temperature or the reduction in pressure, or in addition to an increase in temperature and/or a reduction in pressure, it is also possible to carry out a desorption by stripping the absorption medium loaded with CO₂ by means of a gas.

If, in the desorption of CO₂, water is also removed from the absorption medium, water may be added as necessary to the absorption medium before reuse for absorption.

All apparatus known from the prior art for desorbing a gas from a liquid can be used for the desorption. The desorption is preferably carried out in a desorption column. Alternatively, the desorption of CO₂ may also be carried out in one or more flash evaporation stages.

The desorption is carried out preferably at an absorption medium temperature in the range from 50 to 200°C, more particularly 80 to 180°C. The temperature during desorption is then preferably at least 20°C, more preferably at least 50°C, above the temperature during absorption. The absorption is particularly preferably carried out at a temperature in the range from 0 to 80°C and the desorption is particularly preferably carried out at a higher temperature in the range from 50 to 200°C.

In the case of desorption by lowering the pressure, the desorption of CO₂ is preferably carried out at a total pressure in the gas phase in the range from 0.01 to 10 bar, in particular from 0.1 to 5 bar. The pressure in the desorption is preferably at least 1.5 bar below, particularly preferably at least 4 bar below, the pressure in the absorption and is most preferably atmospheric pressure. The absorption is particularly preferably carried out at a pressure in the range from 0.8 to 90 bar and the desorption is carried out at a lower pressure in the range from 0.01 to 10 bar.

The method of the invention makes it possible to achieve, at the same time, a high absorption capacity for CO₂ and an absorption rate which is sufficiently high for industrial application by use of amines of formula (I). By the use of
5 amines of formula (I), precipitation of a solid can be reliably prevented in the absorption of CO₂, even without addition of a solvent, and phase separation of the absorption medium into two liquid phases can be prevented in the desorption of CO₂. The method of the invention can
10 therefore be used without problems in simply constructed plants as are used in the prior art for gas scrubbing using aqueous solutions of ethanolamine and here achieves an improved absorption performance for CO₂ in comparison with ethanolamine. In addition, discharge of absorbent in the
15 desorption is lower than in the case of ethanolamine.

In a preferred embodiment of the method of the invention, the desorption is carried out first of all by lowering the pressure in one or more successive flash evaporation stages followed by stripping with an inert gas such as air or
20 nitrogen in a desorption column. In the last flash evaporation stages, the pressure is preferably lowered to 1 to 5 bar, more preferably to 1 to 2 bar. The stripping in the desorption column is preferably carried out at a temperature of the absorption medium in the range from 60
25 to 100°C. Flash evaporation combined with stripping enables a low residual content of CO₂ in the absorption medium after desorption to be achieved with a low energy consumption. Thus the amount of absorption medium required in the overall process may be lowered and the need for
30 thermal energy for the desorption of CO₂ may be reduced.

The following examples illustrate the invention without, however, restricting the subject matter of the invention.

Examples

For determining the CO₂ loading, the CO₂ uptake and the relative absorption rate, 150 g of absorption medium consisting of 45 g of amine and 105 g of water were charged to a thermostatable container with a top-mounted reflux condenser cooled at 3°C. After heating to 40°C or 100°C, a gas mixture of 14% CO₂, 80% nitrogen and 6% oxygen by volume was passed at a flow rate of 59 l/h through the absorption medium, via a frit at the bottom of the container, and the CO₂ concentration in the gas stream exiting the reflux condenser was determined by IR absorption using a CO₂ analyser. The difference between the CO₂ content in the gas stream introduced and in the exiting gas stream was integrated to give the amount of CO₂ taken up, and the equilibrium CO₂ loading of the absorption medium was calculated. The CO₂ uptake was calculated as the difference in the amounts of CO₂ taken up at 40°C and at 100°C. From the slope of the curve of CO₂ concentration in the exiting gas stream for an increase in concentration from 1% to 12% by volume, a relative absorption rate of CO₂ in the absorption medium was determined. The amines tested are given in Table 1 with the equilibrium loadings determined in this way at 40°C and 100°C, in mol CO₂/mol amine, the CO₂ uptake in mol CO₂/mol amine, the relative absorption rate of CO₂, relative to Example 1 with 100%, and the boiling point of the amine.

For determining the phase separation temperatures, the absorption medium was heated slowly in a closed, pressure-rated glass container until a clouding or separation into two liquid phases was discernible. An entry marked with the symbol > means that up to that temperature there was no demixing and that the experiment was ended at the temperature indicated, for safety reasons.

The abbreviations used in Table 1 have the following meanings:

MEAs: ethanolamine

TAD: 4-amino-2,2,6,6-tetramethylpiperidine
Pr-TAD: 4-(n-propylamino)-2,2,6,6-tetramethylpiperidine
Bu-TAD: 4-(n-butylamino)-2,2,6,6-tetramethylpiperidine
amine 1:
5 4-(2-hydroxyethylamino)-2,2,6,6-tetramethylpiperidine
amine 2:
4-(2-methoxyethylamino)-2,2,6,6-tetramethylpiperidine
amine 3:
4-(2-hydroxyethylaminoethylamino)-2,2,6,6-tetramethyl-
10 piperidine
amine 4:
4-[bis(2-hydroxyethyl)amino]-2,2,6,6-tetramethylpiperidine
amine 5:
4-(2-piperazinoethylamino)-2,2,6,6-tetramethylpiperidine
15 amine 6:
4-(2-morpholinopropylamino)-2,2,6,6-tetramethylpiperidine

Table 1

Example	Amine	Loading at 40°C in mol/mol	Loading at 100°C in mol/mol	CO ₂ uptake in mol/mol	Relative absorption rate in %	Boiling point of amine in °C at pressure (in mbar)	Phase separation temperature in °C
1*	MEA	0.45	0.22	0.23	100	69 (10)	n.d.
2*	TAD	**	0.54	**	**	79 (10)	n.d.
3*	Pr-TAD	1.53	0.39	1.14	41	102 (14)	70
4*	Bu-TAD	1.38	0.20	1.18	50	251 (1013)	45
5	Amine 1	1.15	0.39	0.76	27	142 (11)	> 90
6	Amine 2	1.13	0.33	0.80	34	117 (12)	116
7	Amine 3	1.56	0.64	0.92	52	166 (3)	> 120
8	Amine 4	1.14	0.37	0.77	28	194 (10)	> 90
9	Amine 5	1.70	0.79	0.91	75	123 (5)	> 145
10	Amine 6	1.26	0.29	0.97	89	113 (1)	124

* not according to the invention

** solid precipitated during introduction of gas
n.d. not determined

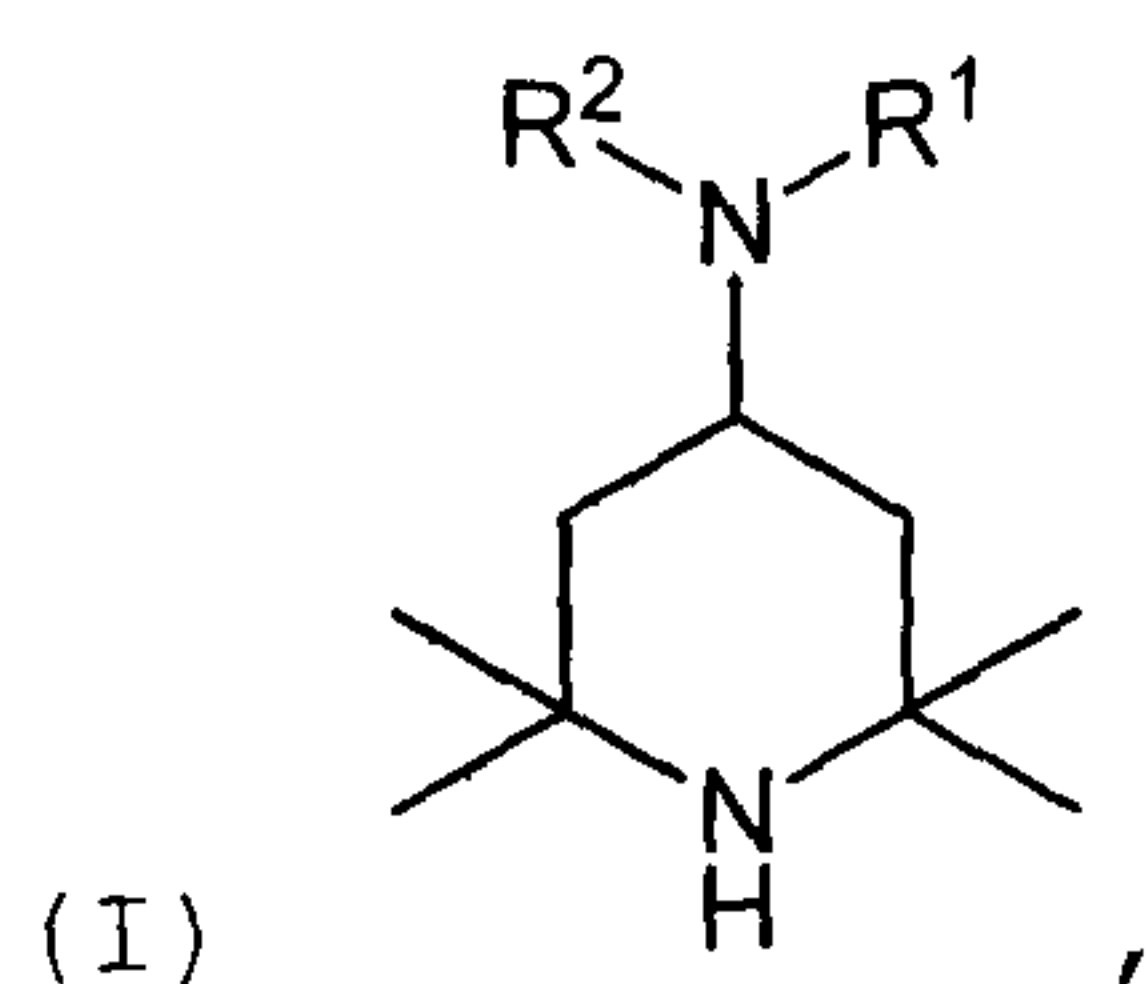
In addition, the corrosion rate of the steel C22 (material number 1.0402) in contact with the absorption medium was determined for the absorption media of Examples 1 and 8 by measurement of the potentiodynamic polarization resistance and interpretation via a Tafel plot using the method
5 ASTM G59-97 (2009). The results are shown in Table 2.

Table 2

Example	Amine	Corrosion rate in mm/year
1	MEA	1.99
8	Amine 4	0.19

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of absorbing CO₂ from a gas mixture by contacting the gas mixture with an absorption medium, wherein the absorption medium comprises water and at least one amine of formula (I)



where

R¹ is a -(CH₂)_n-Y-R³ radical where

R³ = hydrogen or an alkyl radical having from 1 to 6 carbon atoms,

Y is NR³, or Y-R³ is an N-morpholinyl radical or an N-piperazyl radical,

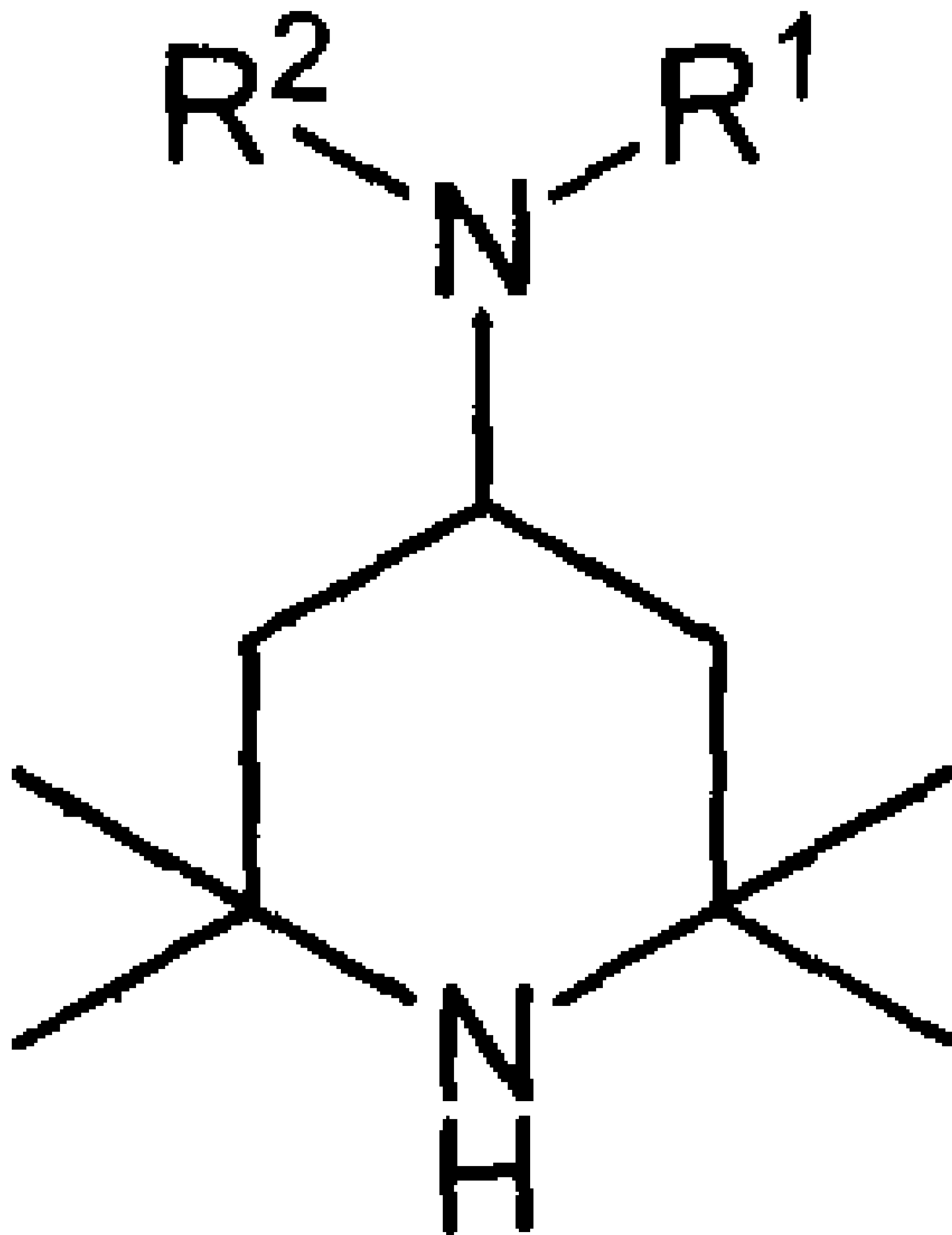
n = 2 to 4, and

R² is hydrogen, an alkyl radical having from 1 to 6 carbon atoms or a radical R¹,

where when R² and R¹ are different, Y-R³ is an N-morpholinyl radical or an N-piperazyl radical.

2. The method according to Claim 1, wherein Y in formula (I) is NR³.
3. The method according to Claim 1, wherein Y-R³ in formula (I) is an N-morpholinyl radical or an N-piperazyl radical.

4. The method according to any one of Claims 1 to 3, wherein n in formula (I) is 2 or 3.
5. The method according to any one of Claims 1 to 4, wherein n in formula (I) is 2.
6. The method according to any one of Claims 1 to 5, wherein the content of amines of formula (I) in the absorption medium is from 10 to 60% by weight.
7. The method according to any one of Claims 1 to 6, wherein the content of amines of formula (I) in the absorption medium is from 20 to 50% by weight.
8. The method according to any one of Claims 1 to 7, wherein the gas mixture is a combustion off-gas, a natural gas or a biogas.
9. The method according to any one of Claims 1 to 8, wherein CO_2 absorbed in the absorption medium is desorbed again by increasing the temperature and/or reducing the pressure and the absorption medium after this desorption of CO_2 is used again for absorbing CO_2 .
10. The method according to Claim 9, wherein the absorption is carried out at a temperature in the range from 0 to 80°C and the desorption is carried out at a higher temperature in the range from 50 to 200°C .
11. The method according to Claim 9 or 10, wherein the absorption is carried out at a pressure in the range from 0.8 to 90 bar and the desorption is carried out at a lower pressure in the range from 0.01 to 10 bar.



(I)