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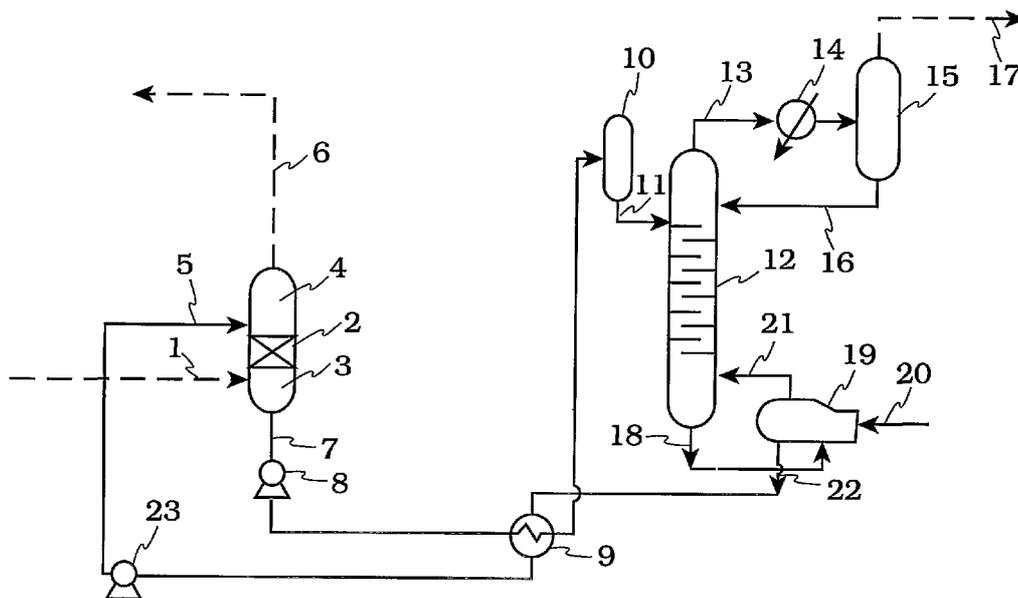
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[Continued on next page]

(54) Title: ABSORBENT COMPOSITION CONTAINING MOLECULES WITH A HINDERED AMINE AND A METAL SULFONATE, PHOSPHONATE OR CARBOXYLATE STRUCTURE FOR ACID GAS SCRUBBING PROCESS

### Adsorption-Regeneration Unit for Selective H<sub>2</sub>S Removal



(57) Abstract: An acid gas absorbent comprising a metal sulfonate, phosphonate or carboxylate of a hindered amine and a process for the selective removal Of H<sub>2</sub>S as well as other acidic components such as carbon disulfide, carbonyl sulfide and oxygen and sulfur derivatives of C1 to C4 hydrocarbons from mixtures containing such acidic components and CO<sub>2</sub> using said absorbent.

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ABSORBENT COMPOSITION CONTAINING MOLECULES WITH A  
HINDERED AMINE AND A METAL SULFONATE, PHOSPHONATE OR  
CARBOXYLATE STRUCTURE FOR ACID GAS SCRUBBING PROCESS

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001] The present invention relates to an absorbent composition and to a process for the selective absorption of H<sub>2</sub>S from an H<sub>2</sub>S and other acidic components containing mixture using the absorbent composition.

DESCRIPTION OF THE RELATED ART

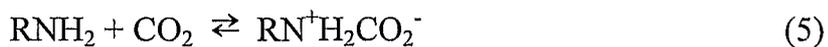
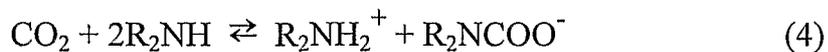
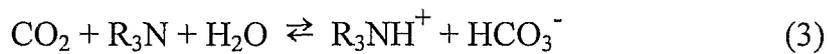
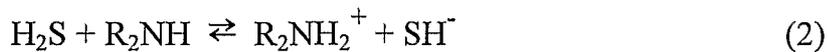
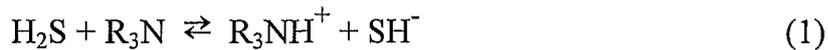
[0002] It is well known in the art to treat gases and liquids, such as mixtures containing acidic gases including CO<sub>2</sub>, H<sub>2</sub>S, CS<sub>2</sub>, HCN, COS and oxygen and sulfur derivatives of C<sub>1</sub> to C<sub>4</sub> hydrocarbons with amine solutions to remove these acidic gases. The amine usually contacts the acidic gases and the liquids as an aqueous solution containing the amine in an absorber tower with the aqueous amine solution contacting the acidic fluid countercurrently.

[0003] The treatment of acid gas mixtures containing, inter alia, CO<sub>2</sub> and H<sub>2</sub>S with amine solutions typically results in the simultaneous removal of substantial amounts of both the CO<sub>2</sub> and H<sub>2</sub>S. For example, in one such process generally referred to as the "aqueous amine process", relatively concentrated amine solutions are employed. A recent improvement of this process involves the use of sterically hindered amines as described in USP 4,112,052, to obtain nearly complete removal of acid gases such as CO<sub>2</sub> and H<sub>2</sub>S. This type of process may be used where the partial pressures of the CO<sub>2</sub> and related gases are low. Another process often used for specialized applications where the partial pressure of CO<sub>2</sub> is extremely high and/or where many acid gases are present, e.g., H<sub>2</sub>S, COS, CH<sub>3</sub>SH and CS<sub>2</sub> involves the use of an amine in combination with a physical absorbent, generally referred to as the "nonaqueous solvent

process". An improvement on this process involves the use of sterically hindered amines and organic solvents as the physical absorbent such as described in USP 4,1 12,051.

[0004] It is often desirable, however, to treat acid gas mixtures containing both CO<sub>2</sub> and H<sub>2</sub>S so as to remove the H<sub>2</sub>S selectively from the mixture, thereby minimizing removal of the CO<sub>2</sub>. Selective removal of H<sub>2</sub>S results in a relatively high H<sub>2</sub>S/CO<sub>2</sub> ratio in the separated acid gas which simplifies the conversion of H<sub>2</sub>S to elemental sulfur using the Claus process.

[0005] The typical reactions of aqueous secondary and tertiary amines with CO<sub>2</sub> and H<sub>2</sub>S can be represented as follows:



wherein each R is an organic radical which may be the same or different and may be substituted with an hydroxy group. The above reactions are reversible, and the partial pressures of both CO<sub>2</sub> and H<sub>2</sub>S are thus important in determining the degree to which the above reactions occur.

[0006] While selective H<sub>2</sub>S removal is applicable to a number of gas treating operations including treatment of hydrocarbon gases from shale pyrolysis, refinery gas and natural gas having a low H<sub>2</sub>S/CO<sub>2</sub> ratio, it is particularly desirable in the treatment of gases wherein the partial pressure of H<sub>2</sub>S is

relatively low compared to that of CO<sub>2</sub> because the capacity of an amine to absorb H<sub>2</sub>S from the latter type gases is very low. Examples of gases with relatively low partial pressures of H<sub>2</sub>S include synthetic gases made by coal gasification, sulfur plant tail gas and low-Joule fuel gases encountered in refineries where heavy residual oil is being thermally converted to lower molecular weight liquids and gases.

**[0007]** Although it is known that solutions of primary and secondary amines such as monoethanolamine (MEA), diethanolamine (DEA), dipropanolamine (DPA), and hydroxyethoxyethylamine (DGA) absorb both H<sub>2</sub>S and CO<sub>2</sub> gas, they have not proven especially satisfactory for preferential absorption of H<sub>2</sub>S to the exclusion of CO<sub>2</sub> because the amines undergo a facile reaction with CO<sub>2</sub> to form carbamates as shown in Equations 5 and 6.

**[0008]** Diisopropanolamine (DIPA) is relatively unique among secondary amino alcohols in that it has been used industrially, alone or with a physical solvent such as sulfolane, for selective removal of H<sub>2</sub>S from gases containing H<sub>2</sub>S and CO<sub>2</sub>, but contact times must be kept relatively short to take advantage of the faster reaction of H<sub>2</sub>S with the amine compared to the rate of CO<sub>2</sub> reaction shown in Equations 2 and 4 hereinabove.

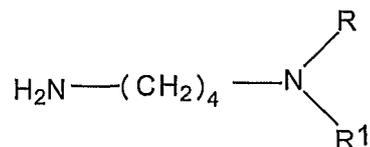
**[0009]** In 1950, Frazier and Kohl, *Ind. and Eng. Chem.*, 42, 2288 (1950) showed that the tertiary amine, methyldiethanolamine (MDEA), has a high degree of selectivity toward H<sub>2</sub>S absorption over CO<sub>2</sub>. This greater selectivity was attributed to the relatively slow chemical reaction of CO<sub>2</sub> with tertiary amines as compared to the rapid chemical reaction of H<sub>2</sub>S. The commercial usefulness of MDEA, however, is limited because of its restricted capacity for H<sub>2</sub>S loading and its limited ability to reduce the H<sub>2</sub>S content to the level at low pressures which is necessary for treating, for example, synthetic gases made by coal gasification.

[0010] Recently, U.K. Patent Publication No. 2,017,524A to Shell disclosed that aqueous solutions of dialkylmonoalkanolamines, and particularly diethylmonoethanolamine (DEAE), have higher selectivity and capacity for H<sub>2</sub>S removal at higher loading levels than MDEA solutions. Nevertheless, even DEAE is not very effective for the low H<sub>2</sub>S loading frequency encountered in the industry. Also, DEAE has a boiling point of 161°C, and as such, it is characterized as being a low-boiling, relatively highly volatile amino alcohol. Such high volatilities under most gas scrubbing conditions result in large material losses with consequent losses in economic advantages.

[0011] U.S. Pat. Nos. 4,405,581; 4,405,583 and 4,405,585 disclose the use of severely sterically hindered amine compounds for the selective removal of H<sub>2</sub>S in the presence of CO<sub>2</sub>. Compared to aqueous methyldiethanolamine (MDEA) severely sterically hindered amines lead to much higher selectivity at high H<sub>2</sub>S loadings.

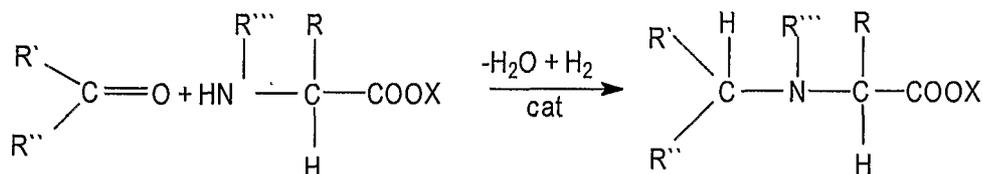
[0012] USP 4,112,052 is directed to a process for removing CO<sub>2</sub> from acid gases using an aqueous amine scrubbing solution. The amines used are sterically hindered amines containing at least one secondary amine group attached to either a secondary or tertiary carbon atom or a primary amino group attached to a tertiary carbon atom. The amines are selected to be at least partially soluble in the solvent used, i.e., water.

[0013] USP 4,376,102 discloses that acidic gases containing CO<sub>2</sub> are removed from normally gaseous mixtures by absorbing the CO<sub>2</sub> from the gaseous mixture using an aqueous solution comprising a basic alkali metal salt or hydroxide which contains (1) at least one diaminoalcohol of the formula



wherein R and R<sup>1</sup> are each independently a C<sub>1</sub>-C<sub>6</sub> alkyl group and either R or R<sup>1</sup> or both R and R<sup>1</sup> have a pendent hydroxyl group and (2) an amino acid. The basic alkali metal salt or hydroxide are selected from the group consisting of alkali metal bicarbonates, carbonates, hydroxides, borates, phosphates and their mixtures. See also USP 4,376,101; USP 4,581,209; USP 4,217,238.

[0014] USP 4,525,294 is directed to amino acid mixtures, their alkali metal salts and processes for their preparation. The process involves the reductive condensation of glycine or alanine and their alkali metal salts with a ketone in the presence of a reductant such as hydrogen and a catalytically effective amount of an hydrogenation catalyst. Thus, a reaction as follows is disclosed:



wherein R is hydrogen or methyl, X is hydrogen or an alkali metal such as sodium or potassium, R' and R'' are selected from the group consisting of:

- a) substituted or unsubstituted linear or branched alkyl radicals having one to 20 carbons; or
- b) substituted or unsubstituted alkylene radicals each having three to six carbon atoms and combined to form a cyclic ring;
- c) substituted or unsubstituted cycloalkyl radicals having from four to eight ring carbon atoms;
- d) substituted or unsubstituted hydroxyl alkyl radicals, linear or branched, having one to 20 carbon atoms; or



thermally decomposable salt of a strong acid, i.e., ammonium salt or a component capable of forming a strong acid and mixtures thereof. Suitable strong acids include inorganic acids such as sulfuric acid, sulfurous acid, phosphoric acid, phosphorous acid, pyrophosphoric acid, an organic acid such as acetic acid, formic acid, adipic acid, benzoic acid, etc. Suitable salts of these acids include the ammonium salts, for example ammonium sulfate, ammonium sulfite, ammonium phosphate and mixtures thereof. Preferably ammonium sulfate (a salt) or  $\text{SO}_2$  (a precursor of an acid) is used as reactant with the amine. Suitable amine salts are those that are non-volatile at conditions used to regenerate the absorbent composition.

[0018] USP 4,892,674 is directed to an absorbent composition comprising an alkaline absorbent solution containing a non-hindered amine and an additive of a severely-hindered amine salt and/or a severely-hindered aminoacid and to the use of the absorbent for the selective removal of  $\text{H}_2\text{S}$  from gaseous streams. The amine salt is the reaction product of an alkaline severely hindered amino compound and a strong acid or a thermally decomposable salt of a strong acid, i.e., ammonium salt. Suitable strong acids include inorganic acids such as sulfuric acid, sulfurous acid, phosphoric acid, phosphorous acid, pyrophosphoric acid; organic acids such as acetic acid, formic acid, adipic acid, benzoic acid, etc. Suitable salts include the ammonium salts, for example, ammonium sulfate, ammonium sulfite, ammonium phosphate and mixtures thereof.

#### DESCRIPTION OF THE FIGURE

[0019] Figure 1 is a diagrammatic flow sheet illustrating an absorption regeneration unit for the selective removal of  $\text{H}_2\text{S}$  from gaseous streams containing  $\text{H}_2\text{S}$  and  $\text{CO}_2$ .

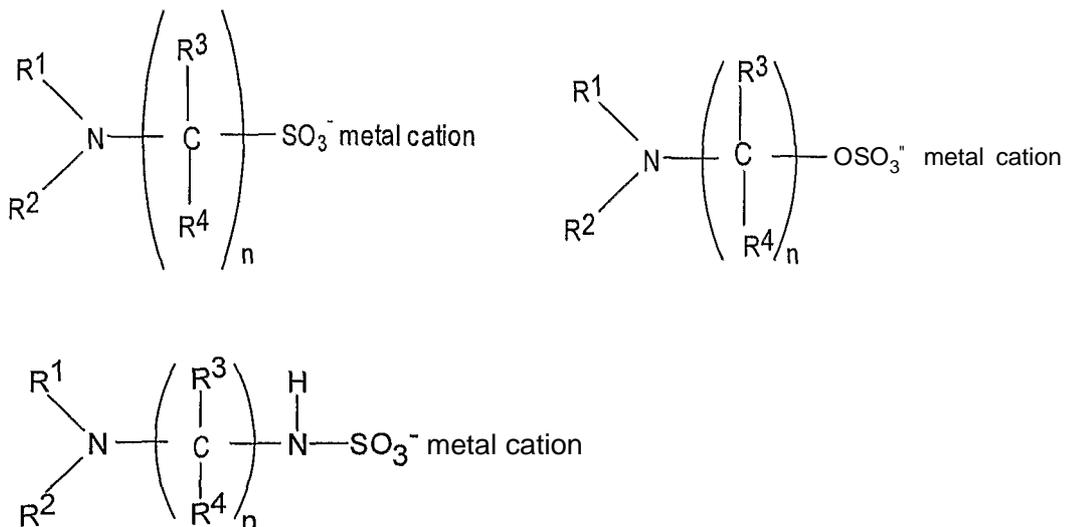
SUMMARY OF THE INVENTION

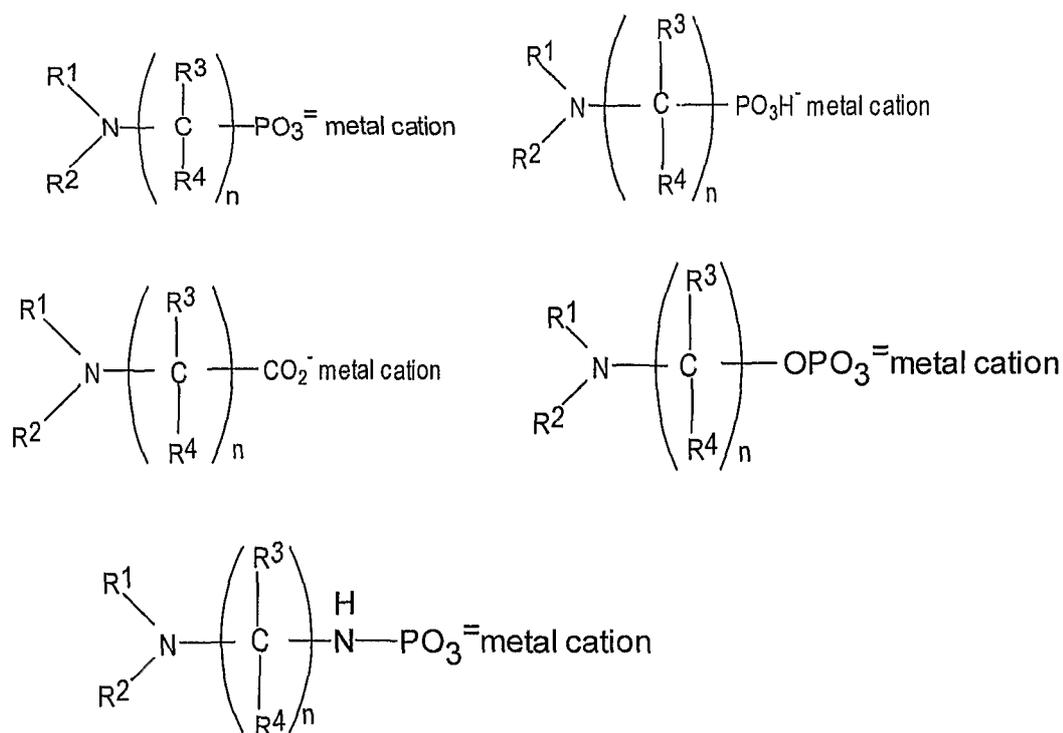
[0020] The present invention is directed to an absorbent comprising a metal sulfonate, metal phosphonate or metal carboxylate of hindered amines and to a method for removing H<sub>2</sub>S from gaseous mixtures containing H<sub>2</sub>S using said absorbents.

DETAILED DESCRIPTION OF THE INVENTION

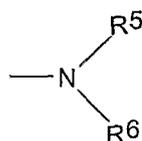
[0021] An absorbent composition comprising at least one of a metal sulfonate, metal phosphonate, metal phosphate, metal sulfamate, metal phosphoramidate or metal carboxylate of at least one hindered secondary or tertiary amine wherein the metal sulfonate, sulfamate, phosphonate, phosphate or phosphoramidate is attached to the amine nitrogen through a group containing at least one chain carbon, preferably 1 to 4 chain carbons, more preferably alkylene group of 2 to 4 chain carbons, and the metal carboxylate is attached to the amine nitrogen through an alkylene group containing 2 or more chain carbons.

[0022] The absorbents are generally represented by the following formulae:





wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are the same or different and selected from H,  $C_1$ - $C_9$  substituted or unsubstituted straight or  $C_3$ - $C_9$  substituted or unsubstituted branched chain alkyl,  $C_3$ - $C_9$  cycloalkyl,  $C_6$ - $C_9$  aryl, alkylaryl, arylalkyl,  $C_2$ - $C_9$  straight or branched hydroxyalkyl, cycloalkyl and mixtures thereof provided both  $R^1$  and  $R^2$  are not hydrogen, and wherein when  $n$  is 2 or more,  $R^3$  and  $R^4$  on adjacent carbon or on carbons separated by one or more carbons can be a cycloalkyl or aryl ring and wherein when substituted the substituents are heteroatom containing substituents, preferably



group wherein  $R^5$  and  $R^6$  are the same or different and are selected from H,  $C_1$ - $C_9$  straight or  $C_3$ - $C_9$  branched chain alkyl,  $C_3$ - $C_9$  cycloalkyl,  $C_6$ - $C_9$  aryl, alkylaryl, arylalkyl,  $C_2$ - $C_9$  straight or branched chain hydroxyalkyl, cycloalkyl and mixtures thereof, provided  $R^5$  and  $R^6$  are not both H, and further wherein,

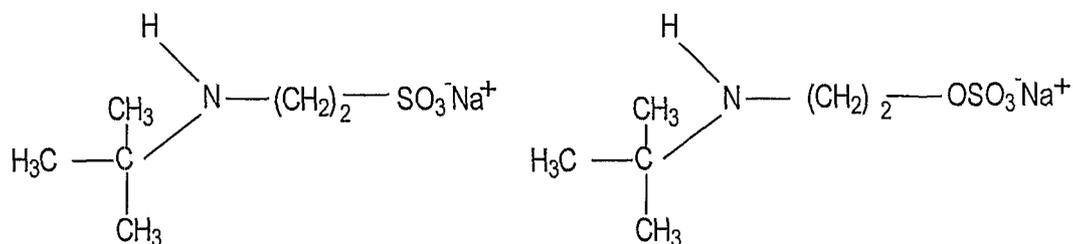
optionally when R<sup>1</sup> is H, and n is 2 or more, R<sup>2</sup> and R<sup>3</sup> or R<sup>4</sup> on the carbon at least one carbon removed from the aminic nitrogen can form a ring,

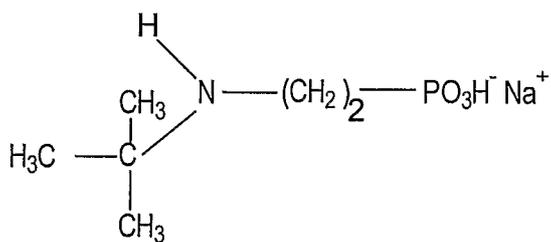
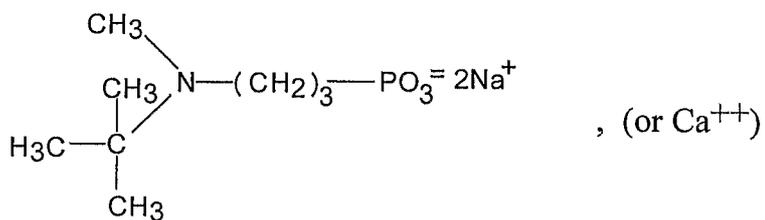
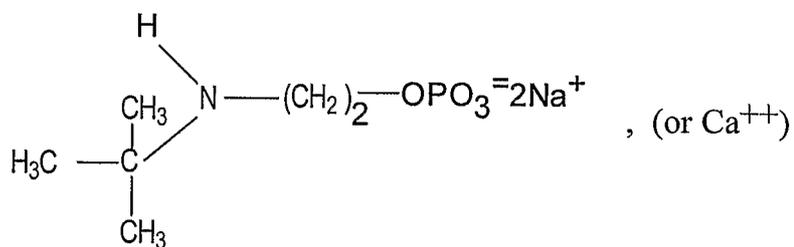
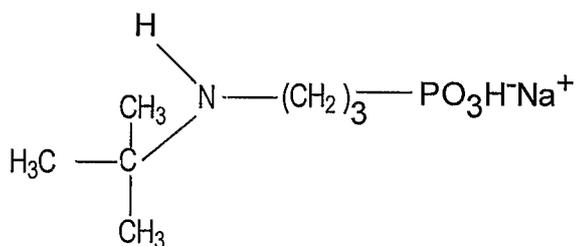
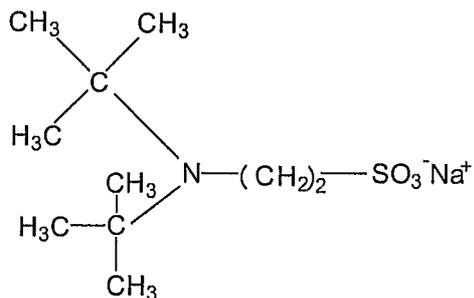
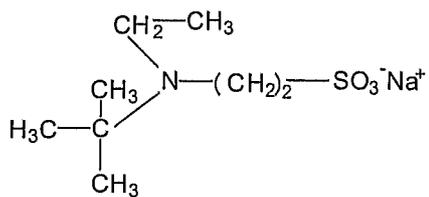
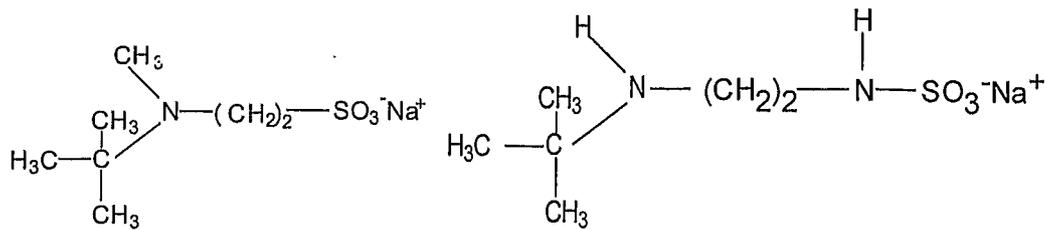
n is an integer of 1 or more, preferably 1 to 4, more preferably 2 to 4, and wherein when n is at least 2 the absorbant can be a metal carboxylate of the amine,

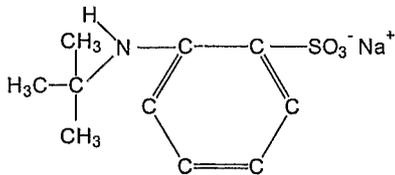
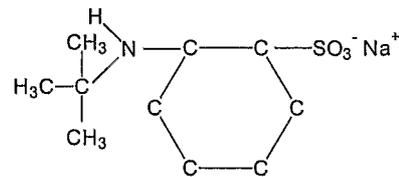
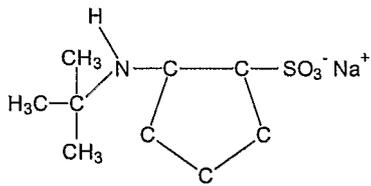
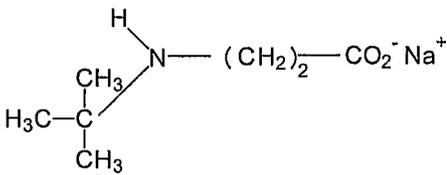
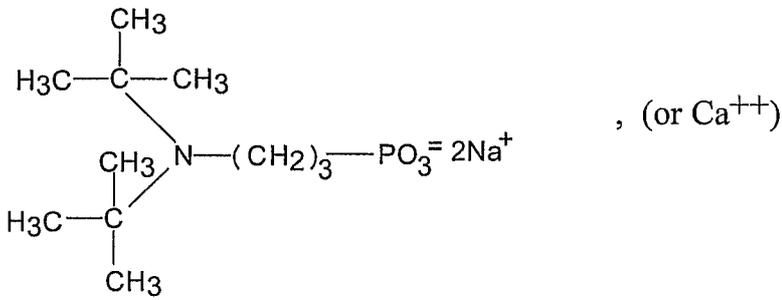
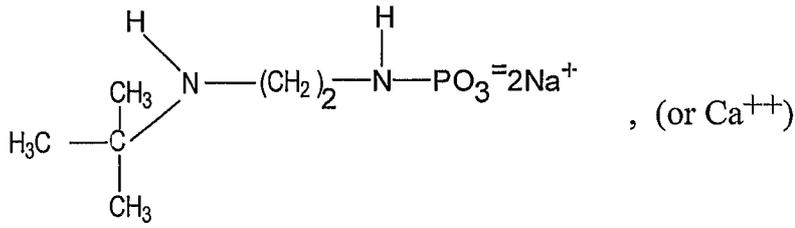
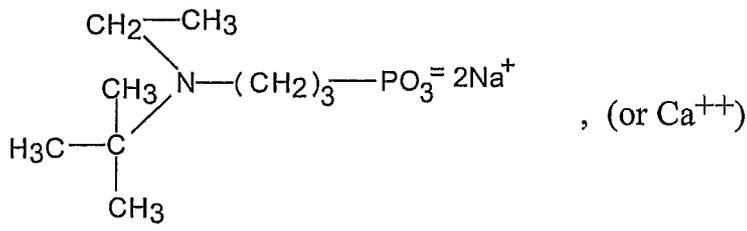
metal cation is one or more monovalent, divalent or trivalent metal cation sufficient to satisfy the valence requirements of the anion or anion cluster, preferably magnesium, barium, aluminum, iron, sodium, lithium, potassium, calcium, nickel, cobalt. Salts formed from divalent cations can be half- or full-salts. Salts formed from trivalent cations can be one third, two third or full salts. By anion cluster is meant 2 or more anions the valence requirements of which are satisfied by, e.g., a single divalent or trivalent metal cation.

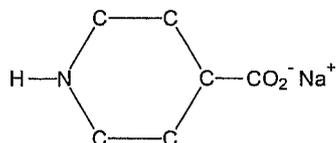
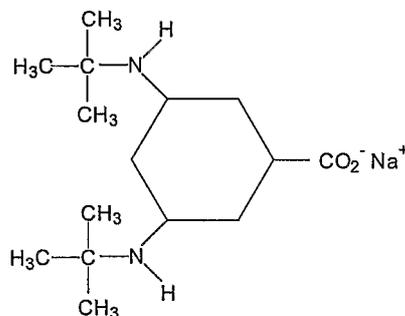
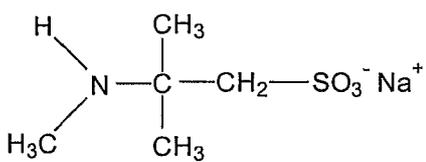
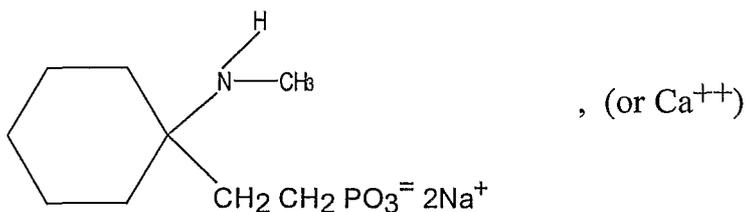
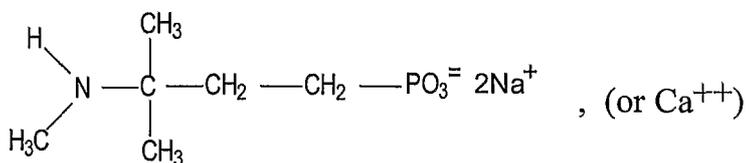
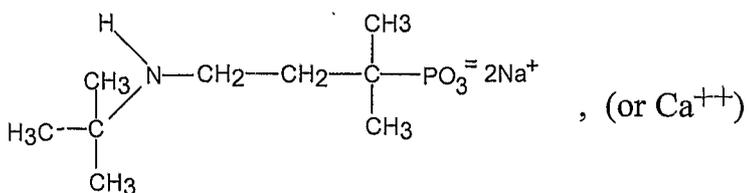
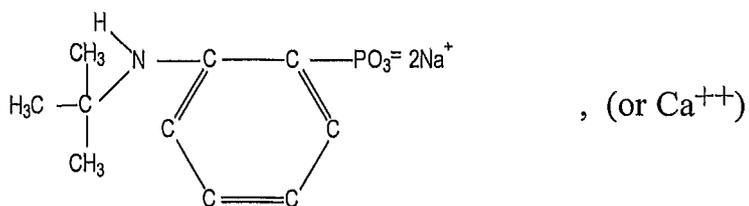
[0023] Preferably R<sup>1</sup> and R<sup>2</sup> are the same or different and are selected from H, C<sub>4</sub>-C<sub>6</sub> substituted or unsubstituted straight or branched chain alkyl, cyclic alkyl, C<sub>6</sub>-C<sub>7</sub> aryl, alkylaryl, arylalkyl C<sub>4</sub>-C<sub>6</sub> straight or branched chain hydroxy alkyl, cycloalkyl and mixtures thereof, more preferably C<sub>4</sub>-C<sub>6</sub> straight or branched chain alkyl, most preferably tertiary-butyl, provided both R<sup>1</sup> and R<sup>2</sup> are not hydrogen.

[0024] Examples of preferred materials are of the formula:









[0025] The absorbents described above exhibit high selectivity for H<sub>2</sub>S and other gaseous acidic component(s) removal from mixtures of said gaseous acidic

components, non-acidic components, and CO<sub>2</sub> and retain their high selectivity and loading capacity even after regeneration.

[0026] The absorbents especially are utilized for the selective absorption of gaseous acid components, e.g., H<sub>2</sub>S from a normally gaseous mixture containing gaseous acidic components, e.g., H<sub>2</sub>S, and non-acidic components and CO<sub>2</sub> comprising:

- (a) contacting said normally gaseous mixture with an absorbent solution characterized as capable of selectively absorbing one or more gaseous acidic components, e.g., H<sub>2</sub>S from said mixture;
- (b) regenerating, at least partially, said absorbent solution containing absorbent gaseous acid components, e.g., H<sub>2</sub>S; and
- (c) recycling the regenerated solution for the selective absorption of one or more gaseous acidic components, e.g., H<sub>2</sub>S by contacting as in step (a).

Preferably, the regenerating step is carried out by heating and stripping and more preferably heating and stripping with steam.

[0027] The term "absorbent solution" as used herein includes but is not limited to solutions wherein the amino compound is dissolved in a solvent selected from water or a physical absorbent or mixtures thereof. Solvents which are physical absorbents (as opposed to the amino compounds which are chemical absorbents) are described, for example, in USP 4,112,051, the entire disclosure of which is incorporated herein by reference, and include, e.g., aliphatic acid amides, N-alkylated pyrrolidones, sulfones, sulfoxides, glycols and the mono- and diethers thereof. The preferred physical absorbents herein are sulfones, and most particularly, sulfolane. The preferred liquid medium comprises water.

[0028] The absorbent solution ordinarily has a concentration of amino compound of about 0.1 to 6 moles per liter of the total solution, and preferably 1 to 4 moles per liter, depending primarily on the specific amino compound

employed and the solvent system utilized. If the solvent system is a mixture of water and a physical absorbent, the typical effective amount of the physical absorbent employed may vary from 0.1 to 5 moles per liter of total solution, and preferably from 0.5 to 3 moles per liter, depending mainly on the type of amino compound being utilized. The dependence of the concentration of amino compound on the particular compound employed is significant because increasing the concentration of amino compound may reduce the basicity of the absorbent solution, thereby adversely affecting its selectivity for H<sub>2</sub>S removal, particularly if the amino compound has a specific aqueous solubility limit which will determine maximum concentration levels within the range given above. It is important, therefore, that the proper concentration level appropriate for each particular amino compound be maintained to insure satisfactory results.

[0029] The solution of this invention may include a variety of additives typically employed in selective gas removal processes, e.g., antifoaming agents, antioxidants, corrosion inhibitors, and the like. The amount of these additives will typically be in the range that they are effective, i.e., an effective amount.

[0030] Also, the amino compounds described herein may be admixed with other amino compounds as a blend. The ratio of the respective amino compounds may vary widely, for example, from 1 to 99 wt% of the amino compounds described herein.

[0031] Three characteristics which are of ultimate importance in determining the effectiveness of the amino compounds herein for H<sub>2</sub>S removal are "selectivity", "loading" and "capacity". The term "selectivity" as used throughout the specification is defined as the following mole ratio fraction:

$$\frac{\text{(moles of H}_2\text{S/moles of CO}_2\text{) in liquid phase}}{\text{(moles of H}_2\text{S/moles of CO}_2\text{) in gaseous phase}}$$

The higher this fraction, the greater the selectivity of the absorbent solution for the H<sub>2</sub>S in the gas mixture.

[0032] By the term "loading" is meant the concentration of the H<sub>2</sub>S and CO<sub>2</sub> gases physically dissolved and chemically combined in the absorbent solution as expressed in moles of gas per moles of the amine. The best amino compounds are those which exhibit good selectivity up to a relatively high loading level. The amino compounds used in the practice of the present invention typically have a "selectivity" of not substantially less than 10 at a "loading" of 0.1 moles, preferably, a "selectivity" of not substantially less than 10 at a loading of 0.2 or more moles of H<sub>2</sub>S and CO<sub>2</sub> per moles of the amino compound.

[0033] "Capacity" is defined as the moles of H<sub>2</sub>S loaded in the absorbent solution at the end of the absorption step minus the moles of H<sub>2</sub>S loaded in the absorbent solution at the end of the desorption step. High capacity enables one to reduce the amount of amine solution to be circulated and use less heat or steam during regeneration.

[0034] The acid gas mixture herein necessarily includes H<sub>2</sub>S, and may optionally include other gases such as CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, CO, H<sub>2</sub>O, COS, HCN, C<sub>2</sub>H<sub>4</sub>, NH<sub>3</sub>, and the like. Often such gas mixtures are found in combustion gases, refinery gases, town gas, natural gas syn gas, water gas, propane, propylene, heavy hydrocarbon gases, etc. The absorbent solution herein is particularly effective when the gaseous mixture is a gas, obtained, for example, from shale oil retort, coal liquefaction or gasification, gasification of heavy oil with steam, air/steam or oxygen/steam, thermal conversion of heavy residual oil to lower molecular weight liquids and gases, e.g., fluid coker, Flexicoker, or delayed coker or in sulfur plant tail gas cleanup operations.

[0035] The absorption step of this invention generally involves contacting the normally gaseous stream with the absorbent solution in any suitable contacting vessel. In such processes, the normally gaseous mixture containing H<sub>2</sub>S and CO<sub>2</sub> from which the H<sub>2</sub>S as well as other acidic components such as carbon disulfide, carbonyl sulfide and oxygen and sulfur derivatives of C<sub>1</sub>-C<sub>4</sub> hydrocarbon can be selectively removed may be brought into intimate contact with the absorbent solution using conventional means, such as a tower or vessel packed with, for example, rings or with sieve plates, or a bubble reactor. Other acidic gaseous components will also be removed.

[0036] In a typical mode of practicing the invention, the absorption step is conducted by feeding the normally gaseous mixture into the lower portion of the absorption tower while fresh absorbent solution is fed into the upper region of the tower. The gaseous mixture, freed largely from the H<sub>2</sub>S, emerges from the upper portion of the tower, and the loaded absorbent solution, which contains the selectively absorbed H<sub>2</sub>S, leaves the tower near or at its bottom. Preferably, the inlet temperature of the absorbent solution during the absorption step is in the range of from about 20°C to about 100°C, and more preferably from 30°C to about 60°C. Pressures may vary widely; acceptable pressures are between 5 and 2000 psia, preferably 20 to 1500 psia, and most preferably 25 to 1000 psia in the absorber. The contacting takes place under conditions such that the H<sub>2</sub>S is selectively absorbed by the solution. The absorption conditions and apparatus are designed so as to minimize the residence time of the liquid in the absorber to reduce CO<sub>2</sub> pickup while at the same time maintaining sufficient residence time of gas mixture with liquid to absorb a maximum amount of the H<sub>2</sub>S gas. The amount of liquid required to be circulated to obtain a given degree of H<sub>2</sub>S removal will depend on the chemical structure and basicity of the amino compound and on the partial pressure of H<sub>2</sub>S in the feed gas. Gas mixtures with low partial pressures such as those encountered in thermal conversion processes

will require more liquid under the same absorption conditions than gases with higher partial pressures such as shale oil retort gases.

[0037] A typical procedure for the selective H<sub>2</sub>S removal phase of the process comprises selectively absorbing H<sub>2</sub>S via countercurrent contact of the gaseous mixture containing H<sub>2</sub>S and CO<sub>2</sub> with the solution of the amino compound in a column containing a plurality of trays at a low temperature, e.g., below 45°C, and at a gas velocity of at least about 0.3 ft/sec (based on "active" or aerated tray surface), depending on the operating pressure of gas, said tray column having fewer than 20 contacting trays, with, e.g., 4-16 trays being typically employed.

[0038] After contacting the normally gaseous mixture with the absorbent solution, which becomes saturated or partially saturated with H<sub>2</sub>S, the solution may be at least partially regenerated so that it may be recycled back to the absorber. As with absorption, the regeneration may take place in a single liquid phase. Regeneration or desorption of the absorbent solution may be accomplished by conventional means such as pressure reduction of the solution or increase of temperature to a point at which the absorbed H<sub>2</sub>S flashes off, or bypassing the solution into a vessel of similar construction to that used in the absorption step, at the upper portion of the vessel, and passing an inert gas such as air or nitrogen or preferably steam upwardly through the vessel. The temperature of the solution during the regeneration step should be in the range from about 50°C to about 170°C, and preferably from about 80°C to 120°C, and the pressure of the solution on regeneration should range from about 0.5 to about 100 psia, preferably 1 to about 50 psia. The absorbent solution, after being cleansed of at least a portion of the H<sub>2</sub>S gas, may be recycled back to the absorbing vessel. Makeup absorbent may be added as needed.

[0039] In the preferred regeneration technique, the H<sub>2</sub>S-rich solution is sent to the regenerator wherein the absorbed components are stripped by the steam

which is generated by re-boiling the solution. Pressure in the flash drum and stripper is usually 1 to about 50 psia, preferably 15 to about 30 psia, and the temperature is typically in the range from about 50°C to 170°C, preferably about 80°C to 120°C. Stripper and flash temperatures will, of course, depend on stripper pressure, thus at about 15 to 30 psia stripper pressures, the temperature will be about 80°C to about 120°C during desorption. Heating of the solution to be regenerated may very suitably be effected by means of indirect heating with low-pressure steam. It is also possible, however, to use direct injection of steam.

[0040] In one embodiment for practicing the entire process herein, as illustrated in Figure 1, the gas mixture to be purified is introduced through line 1 into the lower portion of a gas-liquid countercurrent contacting column 2, said contacting column having a lower section 3 and an upper section 4. The upper and lower sections may be segregated by one or a plurality of packed beds as desired. The absorbent solution as described above is introduced into the upper portion of the column through a pipe 5. The solution flowing to the bottom of the column encounters the gas flowing countercurrently and dissolves the H<sub>2</sub>S preferentially. The gas freed from most of the H<sub>2</sub>S exits through a pipe 6, for final use. The solution, containing mainly H<sub>2</sub>S and some CO<sub>2</sub>, flow toward the bottom portion of the column, from which it is discharged through pipe 7. The solution is then pumped via optional pump 8 through an optional heat exchanger and cooler 9 disposed in pipe 7, which allows the hot solution from the regenerator 12 to exchange heat with the cooler solution from the absorber column 2 for energy conservation. The solution is entered via pipe 7 to a flash drum 10 equipped with a line (not shown) which vents to line 13 and then introduced by pipe 11 into the upper portion of the regenerator 12, which is equipped with several plates and effects the desorption of the H<sub>2</sub>S and CO<sub>2</sub> gases carried along in the solution. This acid gas is passed through a pipe 13 into a condenser 14 wherein cooling and condensation of water and amine

solution from the gas occur. The gas then enters a separator 15 where further condensation is effected. The condensed solution is returned through pipe 16 to the upper portion of the regenerator 12. The gas remaining from the condensation, which contains  $H_2S$  and some  $CO_2$ , is removed through pipe 17 for final disposal (e.g., to a vent or incinerator or to an apparatus which converts the  $H_2S$  to sulfur, such as a Claus unit or a Stretford conversion unit (not shown).

[0041] The solution is liberated from most of the gas which it contains while flowing downward through the regenerator 12 and exits through pipe 18 at the bottom of the regenerator for transfer to a reboiler 19. Reboiler 19, equipped with an external source of heat (e.g., steam injected through pipe 20 and the condensate exits through a second pipe (not shown)), vaporizes a portion of this solution (mainly water) to drive further  $H_2S$  therefrom. The  $H_2S$  and steam driven off are returned via pipe 21 to the lower section of the regenerator 12 and exited through pipe 13 for entry into the condensation stages of gas treatment. The solution remaining in the reboiler 19 is drawn through pipe 22, cooled in heat exchanger 9, and introduced via the action of pump 23 (optional if pressure is sufficiently high) through pipe 5 into the absorber column 2.

[0042] Typically, a gaseous stream to be treated having a 1:10 mole ratio of  $H_2S:CO_2$  from an apparatus for thermal conversion of heavy residual oil, or a Lurgi coal gas having a mole ratio of  $H_2S:CO_2$  of less than 1:10 will yield an acid gas having a mole ratio of  $H_2S:CO_2$  of about 1:1 after treatment by the process of the present invention. The process herein may be used in conjunction with another  $H_2S$  selective removal process; however, it is preferred to carry out the process of this invention by itself, since the amino compounds are extremely effective by themselves in preferential absorption of  $H_2S$ .

## PREPARATION OF TEST SAMPLES

### Preparation of sodium tert-butylaminomethylsulfonate

[0043] 37% Formaldehyde solution (18 g, 0.22 mol) was added to a suspension of sodium bisulfite (22 g, 0.2 mol) in water (25 mL). To this mixture was added tertbutylamine (28 mL, 19.4 g, 0.26 mol) at such a rate that the temperature of the reaction mixture was not exceeding 30°C. When the addition was complete, a distillation apparatus was set and the mixture was stirred at 70-75°C for 10 minutes (excess of tert-butyl amine was distilled off) and cooled to 10-15°C. The formed precipitate was filtered, washed with methanol and dried at 20-25°C to give sodium tert-butylaminomethylsulfonate (30 g, 80%), as white plates, decomposition without melting above 180-190°C (smell of amine),  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  1.02 (s, 9H), 3.32 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  28.9, 49.9, 60.8.

### Sodium 2-(tert-butylamino) ethylsulfonate

[0044] tert-Butylamine (127 mL, 88 g, 1.2 mol) was added to a solution of sodium 2-hydroxyethylsulfonate (29.6 g, 0.2 mol) and disodium phosphate (1.1 g, 8 mmol) in water (50 mL). The mixture was stirred at 240-245°C (6.5 MPa) in an autoclave for 3 hours. The mixture was then cooled to 50-60°C and concentrated to 50 mL under normal pressure. After cooling to 10-15°C, the formed precipitate was filtered, washed with methanol and dried at 20-25°C, yield 10 g. The filtrate was concentrated under normal pressure to approximately 25-30 mL giving an additional 5.6 g of product. Total yield of sodium 2-(tertbutylamino)ethylsulfonate is 15.6 g, 38%, as white plates, decomposition 145-150°C (become semi-fluid),  $^1\text{H}$  NMR (DMSO- $J_6$ )  $\delta$  1.00 (s, 9H), 2.56 (t,  $J = 6.6$  Hz, 2H), 2.72 (t,  $J = 6.6$  Hz, 2H);  $^{13}\text{C}$  NMR  $\delta$  28.9, 38.6, 49.6, 52.2.

3-(tert-Butylamino)propyl sulfonic acid

[0045] To a solution of 1,3-propanesultone (20 g, 0.164 mol) in toluene (100 mL) was added tert-butylamine (90 mL, 62.1 g, 0.85 mol). The mixture was stirred under gentle reflux for 1 hour. The precipitate was filtered, washed with diethyl ether and dried at 20-25°C. Yield 3-(tertbutylamino)propyl sulfonic acid 32 g (approximately 100%), as white microcrystals, mp above 280°C, <sup>1</sup>H NMR (D<sub>2</sub>O) δ 1.33 (s, 9H), 2.07 (p, *J* = 7.6 Hz, 2H), 2.99 (t, *J* = 7.6 Hz, 2H), 3.15 (t, *J* = 7.7 Hz, 2H); <sup>13</sup>C NMR δ 21.3, 24.3, 39.4, 47.4, 56.5.

Sodium 3-(tert-butylamino)propylsulfonate

[0046] 3-(tertButylamino)propyl sulfonic acid (18 g) was added to a solution of sodium hydroxide (3.69 g, 0.092 mol) in methanol (300 mL). The mixture was stirred till become clear. The solvent was removed and the solid residue was dried in vacuum to give sodium 3-(tert-butylamino)propylsulfonate (18.7 g), as white microcrystals, decomposition at 170°C, <sup>1</sup>H NMR (D<sub>2</sub>O) δ 1.08 (s, 9H), 1.80-1.90 (m, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.91-2.96 (m, 2H); <sup>13</sup>C NMR δ 24.4, 26.9, 39.8, 48.7, 49.6.

The preparation of disodium tert-butylaminomethylphosphonate

[0047] *N*-Methylene-tert-butylamine was prepared followed published procedure [USP 2,750,416] with some modifications as follows:

37% Aqueous formaldehyde (89 g of solution, 33 g, 1.1 mol) was added dropwise with stirring to tert-butylamine (73 g, 1 mol) over 20 minutes keeping the temperature below 20°C (cooling on ice-bath). The reaction mixture was stirred for 30 minutes at 20-22°C, cooled to 5-10°C and potassium hydroxide (30 g) was added portionwise with cooling at 15-20°C. The organic layer was separated and dried over potassium hydroxide pellets. The attempted purification by distillation gave unsatisfactory results due to trimerization of

*N*-methylene-*tert*-butylamine at elevated temperature. The purification of the crude product was achieved by the distillation in the presence of catalytic *p*-toluenesulfonic acid (on 10 cm column, oil-bath 115-120°C) to give pure *N*-methylene-*tert*-butylamine in 87% yield (74 g), bp 66-67 °C (lit. [USP 2,750,416] 64-65 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.20 (s, 9H), 7.26 (d, *J* = 16.0 Hz, 1H), 7.41 (d, *J* = 16.0 Hz, 1H).

#### Diethyl *tert*-butylaminomethylphosphonate

[0048] Diethyl phosphite (41.4 g, 0.3 mol) was added to *N*-methylene-*tert*-butylamine (25.6 g, 0.3 mol) under nitrogen atmosphere. Within 1-2 minutes the temperature of the mixture spontaneously rose to 60-70°C. The mixture was stirred at 80°C for 30 minutes and then at 20-25°C for 12 hours. The NMR test of the mixture showed pure diethyl *tert*-butylaminomethylphosphonate, as a colorless oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.08 (s, 9H), 1.34 (t, *J* = 7.0 Hz, 6H), 2.93 (d, *J* = 15.1 Hz, 2H), 4.1-4.22 (m, 4H); <sup>13</sup>C NMR δ 16.4 (d, *J* = 5.7 Hz), 28.4, 38.6 (d, *J* = 159.2 Hz), 50.8 (d, *J* = 17.8 Hz), 62.1 (d, *J* = 6.9 Hz). "Novel Synthesis of Aminomethyl Phosphoric Acid, Moedritzer, K., Synthesis in Inorganic and Metal-Organic Chemistry, 1972, 2, 317.

#### *tert*-Butylaminomethylphosphonic acid

[0049] The above crude ester (65 g) was added dropwise to concentrated hydrochloric acid (200 mL). The mixture was stirred at 90°C for 20 hours. The mixture was concentrated in vacuum to solidifying and ethanol (300 mL) was added to the residue. The mixture was cooled to -5°C for 30 minutes. The precipitate was filtered and washed with diethyl ether to give 44 g (90%) of crude acid (contaminated with adsorbed hydrogen chloride).

[0050] The crude acid was dissolved in boiling water (60 mL) followed by the addition of methanol (500 mL) and immediately propylene oxide (20 mL).

The mixture was cooled to  $-5^{\circ}\text{C}$  for 1 hour, and the precipitate was filtered and washed with methanol and diethyl ether to give 40.5 g of *tert-butylamino*-methylphosphonic acid, white needles, mp  $295^{\circ}\text{C}$  decomposition (Moedritzer, K., op cit)  $289^{\circ}\text{C}$  decomposition);  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  1.31 (s, 9H), 3.03 (d,  $J = 13.9$  Hz, 2H);  $^{13}\text{C}$  NMR  $\delta$  23.9, 37.6 (d,  $J = 137\text{A}$  Hz), 58.1 (d,  $J = 7.4$  Hz).

#### Disodium *tert*-butylaminomethylphosphonate

[0051] *tert*-Butylaminomethylphosphonic acid (18.4 g, 0.11 mol) was added to sodium hydroxide (8.8 g, 0.22 mol) solution in methanol (100 mL). The mixture was stirred under reflux for 2 hours. The mixture was concentrated in vacuum until solidifying (approximately to 1/3 of volume) and diethyl ether was added (200 mL). The precipitate was filtered and washed with diethyl ether to give disodium *tert*-butylaminomethylphosphonate (20 g, 86%), white micro-crystals, decomposition  $350\text{-}400^{\circ}\text{C}$ ;  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  1.02 (s, 9H), 2.47 (d,  $J = 15.0$  Hz, 2H);  $^{13}\text{C}$  NMR  $\delta$  26.4, 40.1 (d,  $J = 136.3$  Hz), 50.6 (d,  $J = 12.0$  Hz).

#### EXPERIMENTAL PROCEDURE

1. Absorption tests were carried out at  $35^{\circ}\text{C}$  on 0.15 M aqueous solutions of absorbent using a gas mixture of nitrogen: carbon dioxide :hydrogen sulfide of 89: 10:1 for 2 hours.
2. Desorption experiments were run at  $85^{\circ}\text{C}$  in flowing nitrogen for 2 hours at the same flow rate as the test gas mixture.

[0052] The absorbents tested and the absorption results of both fresh absorbent and regenerated absorbent are presented in Table 1.

TABLE 1

	Compound	Molecular weight	Selectivity	Loading (%)	Capacity (%)	Selectivity Reabsorption
1	TBA-CH <sub>2</sub> -SO <sub>3</sub> Na	189.21	14.4	5.4	71	4.5
2	TBA-(CH <sub>2</sub> ) <sub>2</sub> -SO <sub>3</sub> Na	203.24	34.9	13.3	82	22.5
3	TBA-(CH <sub>2</sub> ) <sub>3</sub> -SO <sub>3</sub> Na	217.26	20.4	14.9	54	29.5
4	TBA-(CH <sub>2</sub> ) <sub>3</sub> -SO <sub>3</sub> H	196.29	1.2	0.2	--	--
5	TBA-CH <sub>2</sub> -PO <sub>3</sub> H <sub>2</sub> , Et <sub>3</sub> N	369.5	--	--	--	--
6	TBA-(CH <sub>2</sub> )-PO <sub>3</sub> <sup>-</sup> Na <sub>2</sub> <sup>+</sup>	314	103.8	17.8	22.6	92.41
7	TBA-(CH <sub>2</sub> ) <sub>2</sub> -PO <sub>3</sub> H <sub>2</sub> , Et <sub>3</sub> N	383.55	0.2	25.1	--	--
8	TBA-(CH <sub>2</sub> ) <sub>2</sub> -PO <sub>3</sub> <sup>-</sup> Na <sub>2</sub> <sup>+</sup>	328	107.2	14.2	52.2	81.8
9	TBA-(CH <sub>2</sub> ) <sub>3</sub> -PO <sub>3</sub> H <sub>2</sub> , Et <sub>3</sub> N	397.58	0.4	25.7	--	--
10	TBA-(CH <sub>2</sub> ) <sub>3</sub> -PO <sub>3</sub> <sup>-</sup> Na <sub>2</sub> <sup>+</sup>	342	59.9	14.5	29.8	47.8
11	TBA-(CH <sub>2</sub> ) <sub>4</sub> -PO <sub>3</sub> H <sub>2</sub> , Et <sub>3</sub> N	411.60	0.8	--	--	--
12	TBA-(CH <sub>2</sub> ) <sub>4</sub> -PO <sub>3</sub> <sup>-</sup> Na <sub>2</sub> <sup>+</sup>	356.08	67.2	15.6	63.5	78.6
13	TBA-CH <sub>2</sub> -CO <sub>2</sub> Na <sup>+</sup>	153.15	10.8	33.0	69.3	18.3
14	TBA-(CH <sub>2</sub> ) <sub>3</sub> -CO <sub>2</sub> Na <sup>+</sup>	181.21	19.3	30.8	49.3	16.8
15	EETB (USP 4,405,585)	161.24	15.4 12.6 15.6	16.3 19.1 16.7	60 58 64	13.3 11.2 21.5

Selectivity = (H<sub>2</sub>S/CO<sub>2</sub>) in solution / (H<sub>2</sub>S/CO<sub>2</sub>) in feed gas

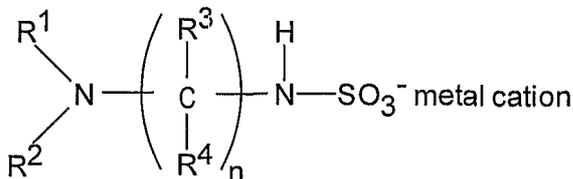
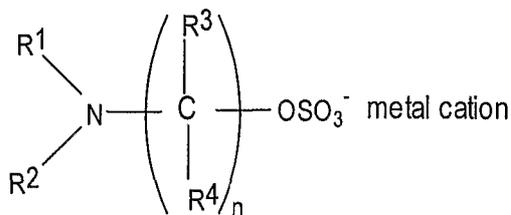
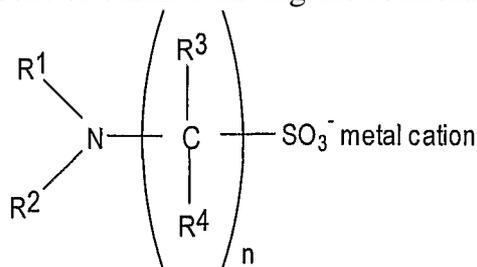
Loading = Moles of H<sub>2</sub>S / Moles of absorbent compound

Capacity = 
$$\frac{\text{Moles of H}_2\text{S absorbed by absorbent solution} / \text{Moles of H}_2\text{S remaining after desorption from solution}}{\text{Moles of H}_2\text{S absorbed by absorbent solution}}$$

## CLAIMS:

1. Absorbents for the selective absorption of normally gaseous acidic components from mixtures containing said gaseous acidic component and gaseous non-acidic components and CO<sub>2</sub> said absorbents comprising a metal sulfonate, metal sulfate, metal sulfamate, metal phosphonate, metal phosphate metal phosphoramidate or metal carboxylate of at least one hindered secondary or tertiary amine wherein the metal sulfonate, sulfate, sulfamate, phosphonate, phosphate or phosphoramidate is attached to the amine nitrogen through a group containing at least one chain carbon and the metal carboxylate is attached to the amine nitrogen through an alkylene group containing at least 2 chain carbons.

2. The absorbent of claim 1 having the formula



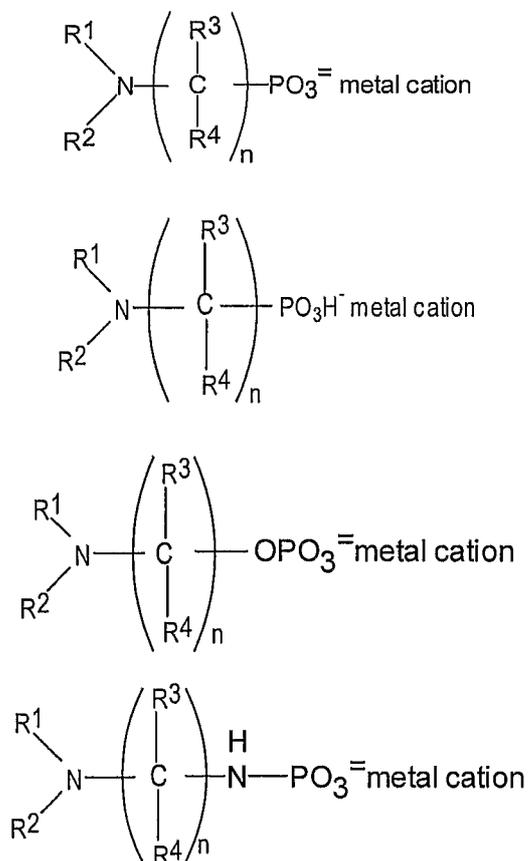
wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are the same or different and selected from hydrogen, C<sub>1</sub>-C<sub>9</sub> substituted or unsubstituted alkyl, C<sub>3</sub>-C<sub>9</sub> substituted or unsubstituted branched chain alkyl, C<sub>3</sub>-C<sub>9</sub> cycloalkyl, C<sub>6</sub>-C<sub>9</sub> aryl, alkylaryl or arylalkyl, C<sub>2</sub>-C<sub>9</sub> straight or branched hydroxyalkyl, hydroxy cycloalkyl and mixtures thereof

provided both R<sup>1</sup> and R<sup>2</sup> are not hydrogen; and wherein when n is 2 or more, R<sup>3</sup> and R<sup>4</sup> on adjacent carbon or on carbons separated by one or more carbons can be a cycloalkyl or aryl ring and wherein when substituted the substituents are heteroatom containing substituents,

n is an integer of 1 or more, and

metal cation is a monovalent, divalent or trivalent metal cation sufficient to satisfy the valence requirements of the anion or anion cluster.

3. The absorbent of claim 1 having the formula



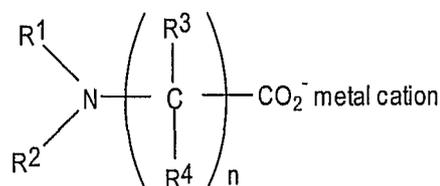
wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are the same or different and selected from hydrogen, C<sub>1</sub>-C<sub>9</sub> substituted or unsubstituted alkyl, C<sub>3</sub>-C<sub>9</sub> substituted or unsubstituted branched chain alkyl, C<sub>3</sub>-C<sub>9</sub> cycloalkyl, C<sub>6</sub>-C<sub>9</sub> aryl, alkylaryl or arylalkyl, C<sub>2</sub>-C<sub>9</sub> straight or branched hydroxyalkyl, hydroxy cycloalkyl and mixtures thereof

provided both R<sup>1</sup> and R<sup>2</sup> are not hydrogen; and wherein when n is 2 or more, R<sup>3</sup> and R<sup>4</sup> on adjacent carbon or on carbons separated by one or more carbons can be a cycloalkyl or aryl ring and wherein when substituted the substituents are heteroatom containing substituents,

n is an integer of 1 or more, and

metal cation is a monovalent, divalent or trivalent metal cation sufficient to satisfy the valence requirements of the anion or anion cluster.

4. The absorbent of claim 1 having the formula



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are the same or different and selected from hydrogen, C<sub>1</sub>-C<sub>9</sub> substituted or unsubstituted alkyl, C<sub>3</sub>-C<sub>9</sub> substituted or unsubstituted branched chain alkyl, C<sub>3</sub>-C<sub>9</sub> cycloalkyl, C<sub>6</sub>-C<sub>9</sub> aryl, alkylaryl or arylalkyl, C<sub>2</sub>-C<sub>9</sub> straight or branched hydroxyalkyl, hydroxy cycloalkyl and mixtures thereof provided both R<sup>1</sup> and R<sup>2</sup> are not hydrogen; and wherein when n is 2 or more, R<sup>3</sup> and R<sup>4</sup> on adjacent carbon or on carbons separated by one or more carbons can be a cycloalkyl or aryl ring and wherein when substituted the substituents are heteroatom containing substituents,

n is an integer of 2 or more, and

metal cation is one or more monovalent, divalent or trivalent metal cation sufficient to satisfy the valence requirement of the anion or anion cluster.

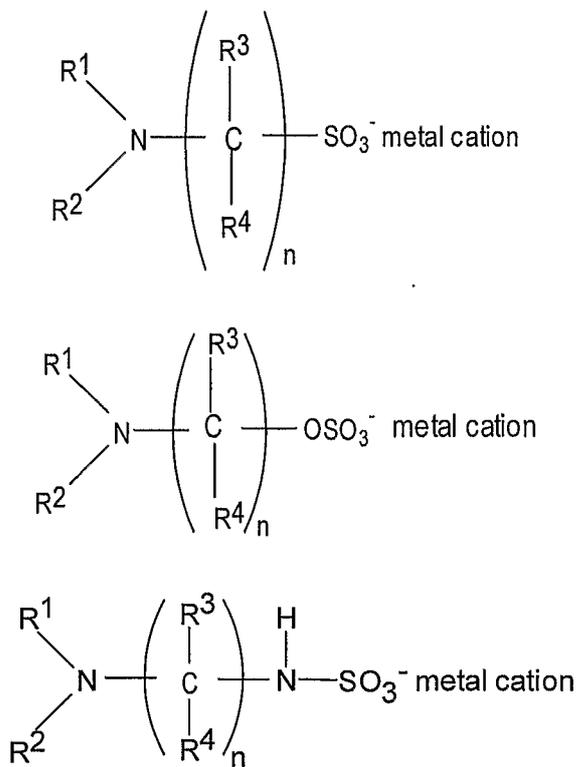
5. A process for the selective absorption of one or more gaseous acidic components from gaseous mixtures of said acidic components and non-acidic

components and CO<sub>2</sub> by contacting said mixture with an absorbent amino-containing solution comprising:

a metal sulfonate, metal sulfate, metal sulfamate, metal phosphonate, metal phosphate or metal phosphoramidate of at least one hindered secondary or tertiary amine wherein the metal sulfonate, sulfate, sulfamate, phosphonate, phosphate or phosphoramidate is attached to the amine nitrogen through an alkylene group containing at least one carbon,

under conditions whereby the gaseous acidic component is selectively absorbed from said mixture.

6. The process of claim 5 wherein the absorbent solution comprises an absorbent having the formulae:



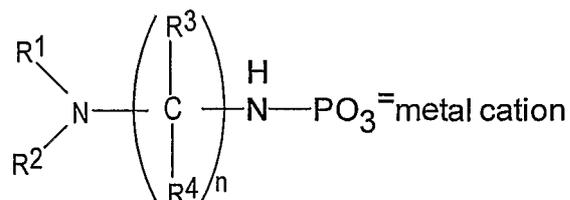
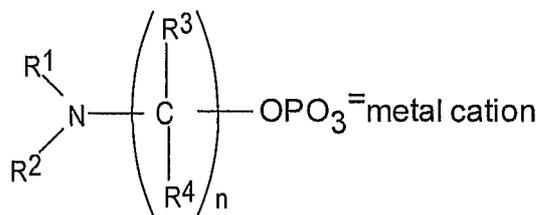
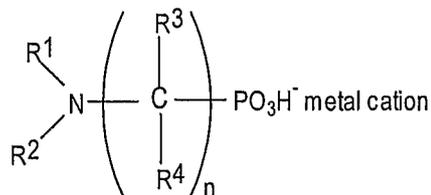
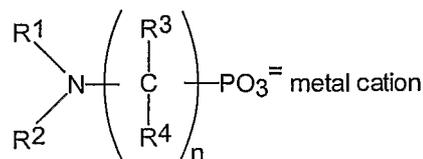
wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are the same or different and selected from hydrogen, C<sub>1</sub>-C<sub>9</sub> substituted or unsubstituted alkyl C<sub>3</sub>-C<sub>9</sub> substituted or unsubstituted

branched chain alkyl, C<sub>3</sub>-C<sub>9</sub> cycloalkyl, C<sub>6</sub>-C<sub>9</sub> aryl, alkylaryl or arylalkyl, C<sub>3</sub>-C<sub>9</sub> straight or branched hydroxyalkyl, hydroxy cycloalkyl and mixtures thereof provided both R<sup>1</sup> and R<sup>2</sup> are not hydrogen; and wherein when n is 2 or more, R<sup>3</sup> and R<sup>4</sup> on adjacent carbon or on carbons separated by one or more carbons can be a cycloalkyl or aryl ring and wherein when substituted the substituents are heteroatom containing substituents,

n is an integer of 1 or more, and

metal cation is a monovalent, divalent or trivalent metal cation sufficient to satisfy the valence requirement of the anion or anion cluster.

7. The process of claim 5 wherein the absorbent solution comprises an absorbent having the formulae

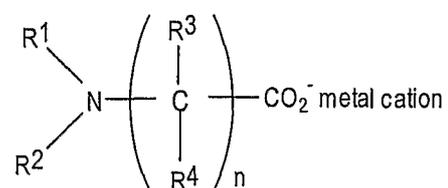


wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are the same or different and selected from hydrogen, Ci-C<sub>9</sub> substituted or unsubstituted alkyl C<sub>3</sub>-C<sub>9</sub> substituted or unsubstituted branched chain alkyl, C<sub>3</sub>-C<sub>9</sub> cycloalkyl, C<sub>6</sub>-C<sub>9</sub> aryl, alkylaryl or arylalkyl, C<sub>3</sub>-C<sub>9</sub> straight or branched hydroxyalkyl, hydroxy cycloalkyl and mixtures thereof provided both  $R^1$  and  $R^2$  are not hydrogen; and wherein when n is 2 or more,  $R^3$  and  $R^4$  on adjacent carbon or on carbons separated by one or more carbons can be a cycloalkyl or aryl ring and wherein when substituted the substituents are heteroatom containing substituents,

n is an integer of 1 or more, and

metal cation is a monovalent, divalent or trivalent metal cation sufficient to satisfy the valence requirement of the anion or anion cluster.

8. The process of claim 5 wherein the absorbent solution comprises and absorbent having the formula



wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are the same or different and selected from hydrogen, Ci-C<sub>9</sub> substituted or unsubstituted alkyl C<sub>3</sub>-C<sub>9</sub> substituted or unsubstituted branched chain alkyl, C<sub>3</sub>-C<sub>9</sub> cycloalkyl, C<sub>6</sub>-C<sub>9</sub> aryl, alkylaryl or arylalkyl, C<sub>2</sub>-C<sub>9</sub> straight or branched hydroxyalkyl, hydroxy cycloalkyl and mixtures thereof provided both  $R^1$  and  $R^2$  are not hydrogen; and wherein when n is 2 or more,  $R^3$  and  $R^4$  on adjacent carbon or on carbons separated by one or more carbons can be a cycloalkyl or aryl ring and wherein when substituted the substituents are heteroatom containing substituents,

n is an integer of 2 or more, and

metal cation is one or more monovalent, divalent or trivalent metal cation sufficient to satisfy the valence requirement of the anion or anion cluster.

9. The process of claim 5 wherein the gaseous acidic component selectively absorbed by the absorbent is H<sub>2</sub>S.

10. The process of claim 6 wherein the gaseous acidic component selectively absorbed by the absorbent is H<sub>2</sub>S.

11. The process of claim 7 wherein the gaseous acidic component selectively absorbed by the absorbent is H<sub>2</sub>S.

12. The process of claim 8 wherein the gaseous acidic component selectively absorbed by the absorbent is H<sub>2</sub>S.



EVTERNATIONAL SEARCH REPORT

International application No

PCT/US06/29894

**A CLASSIFICATION OF SUBJECT MATTER**

IPC **C10G 21/20( 2007 01),C09K 3/00( 2007 01),C07C 211/09( 2007 01),C07D 251/04( 2007 01),B01D 53/34( 2007 01),3/10( 2007 01),3/34( 2007 01),3/42( 2007 01),C09K 3/00( 2007 01),E21B 43/26( 2007 01)**  
COIB 21/00( 2007 01),17/00( 2007 01),B01D 47/00( 2007 01),C07F 9/24( 2007 01),B01J 31/00( 2007 01)

USPC 252/60, 192, 189, 190,423/220,223,226,228,229,232,203/2,58,60,6 1,62,63,9 1,159/47 1

According to International Patent Classification (IPC) or to both national classification and IPC

**B FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U S 252/60,192,189,190,423/220,223,226,228,229,232,203/2,58,60,61,62,63,91,159/47 1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Hawley's Condensed Chemical Dictionary, Advanced Organic Chemistry, Aldrich Advancing Science

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 3,296,170 (Burkhart et al) 3 January 1967 (03 01 1967), Col 3, line 55,57	1,2
X	US 3,065,104 (Kane) 20 November 1962 (20 9 1962), Col 2, line 45-54	1,2,4
X	US 6,844,297 B2 (Allan et al) 18 January 2005 (18 01 2005), Col 1, line 45-46	1,4
X	US 3,321,273 (Fishcher) 23 May 1967 (23 05 1967), Col 1, line 12-14	1,2
X	US 3,133,950 (Pizzarello et al) 19 May 1964 (19 05 1964), Col 1, line 21-26, Col 2, line 35-38, formula of Examples	1,2
X	US 5,143,585 A (Ichikawa et al) 1 September 1992 (01 09 1992), Col 6, line 11-12	1,2,3
Y	GB 1,058,304 A (Manmohan) 11 March 1965 (11 03 1965), page 1, line 25-27 Abstract	1-4

Further documents are listed in the continuation of Box C  See patent family annex

*	Special categories of cited documents	'T'	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A	document defining the general state of the art which is not considered to be of particular relevance	'X'	document of particular relevance the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
'E'	earlier application or patent published on or after the international filing date	Y	document of particular relevance the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents such combination being obvious to a person skilled in the art
'L'	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	'&'	document member of the same patent family
'O'	document referring to an oral disclosure use exhibition or other means		
'P'	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search: 08 November 2006 (08 11 2006) Date of mailing of the international search report: 08 JAN 2007

Name and mailing address of the ISA/US: Mail Stop PCT, Attn ISA/US, Commissioner for Patents, P O Box 145C, Alexandria, Virginia 22313-1450  
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Telephone No 571-272-2100

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US06/29894

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,240,922 (Sartori et al) 23 December 1980 (23.12.1980), Abstract, line 14-19.	1-4
Y	US 4,112,050 (Sartori et al) 5 September 1978 (05.09.1978), Col. 10-18	1-4
Y	US 4,405,583 (Stogryn et al) 20 September 1983 (20.09.1983), Col. 3, line 3-5, Col. 5, line 12-50, Abstract.	1-4
Y	US 4,618,481 (Heinzelmann et al) 21 October 1986 (21.10.1986), Abstract.	1-4
Y	US 5,807,913 A (Mikuni et al) 15 September 1998 (15.09.1998), Abstract.	1,3
Y	US 2,288,749 (Schulze) 7 July 1942 (07.07.1942), Example	1,2
Y	US 3,057,896 (Schlicht et al) 09 October 1962 (09.10.1962), Col. 1, line 19-22, 45-64.	1,2
Y	US 6,872,371 (Hakka et al) 29 March 2005 (03.29.2005), Col. 3, line 44-46.	1,2
Y	US 3,265,710 (Ayers et al) 9 August 1966 (09.08.1966), Col. 9, line 35-49.	1,2
Y	US 5,779,998 A (Tom) 14 July 1998 (14.07.1998), Col. 12, line 32-33.	1,4
Y	US 4,519,994 (Smalheiser) 28 May 1985 (28.05.1985), Col. 1, line 29-35.	1,3
Y	US 20040254066 A1 (Ramarao et al) 16 December 2004 (16.12.2004), page 18, claim 6.	1,3