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PATENT SPECIFICATION



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461001

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Complete Specification Accepted: Feb. 2, 1937.

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PROVISIONAL SPECIFICATION

Improvements in the Removal of Organically Combined Sulphur from Gases

I, JAMES YATE JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfurt - on - Main, Germany, a Joint Stock Company, organized under the Laws of Germany), to be as follows:—

It is already known that organically combined sulphur in gases is frequently very troublesome, especially when the gases are to be subjected to catalytic processes.

Among the processes hitherto proposed for the removal of the organically combined sulphur, the catalytic conversion of the organically combined sulphur into hydrogen sulphide has so far proved the most efficient. Catalysts are employed which contain heavy metals, in particular iron, lead, molybdenum, nickel or tungsten, or advantageously molybdenum or tungsten sulphide. This process has the drawback that comparatively high temperatures of from 300° to 600° Centigrade must be employed.

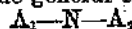
It has also been proposed to lead the gases at about 200° Centigrade over a metal of the 5th, 6th or 7th group of the periodic system which contains a metal of another group, the exhausted metallic mass being regenerated by treatment with oxygen-containing gases at about 450° Centigrade. This process is comparatively troublesome and expensive.

It has also been proposed to remove organically combined sulphur from gases by treating them with alcoholic alkaline solutions but this method is unsuitable for industrial purposes because carbon dioxide is always contained in the gases and is also absorbed by the alkaline solutions whereby great waste of solution is occasioned.

My foreign correspondents have now found that organically combined sulphur, such as carbon disulphide and especially carbon oxysulphide, can be removed from gases by bringing the gas to be purified into contact with strong organic bases or

basic-reacting salts of strong inorganic or organic bases at such high temperatures that the organically combined sulphur is converted into hydrogen sulphide which is led away from the purifying agent together with the gas.

The basic substances which may be employed according to this invention are divisible into three groups. The first group comprises the organic bases among which are all strongly basic amines and especially those containing hydroxyl groups. Tetramethylammonium hydroxide, monoethanolamine, diethanolamine, triethanolamine, butyldiethanolamine and dimethylethanolamine may be mentioned by way of example. Still stronger basic amines which contain more than 20 per cent. of nitrogen and more than one nitrogen atom, as for example diamino-isopropanol, may also be employed. The use of bases containing at least two atoms of nitrogen in the molecule and corresponding to the general formula:



B



(in which B is an aliphatic hydrocarbon radicle which may also contain a simple or substituted amino group and in which at least one of the groups A is an alkyl or aryl group which may contain a hydroxyl group or a simple or substituted amino group or at least one of the groups A is a simple or substituted group, or in which two groups A attached to different nitrogen atoms constitute an alkylene group while each of the remaining groups A is hydrogen or an alkyl or aryl group) offers special advantages. Bases of the said kind are advantageously derived from readily accessible unsaturated hydrocarbons, such as ethylene or propylene. There may be mentioned in particular the substitution products of ethylene diamine, diethylene triamine, triethylene tetramine and tetraethylene pentamine and the corresponding derivatives of triamino-propylene, triaminobutylene and tetraaminobutylene. As suitable substances

[Price 1/-]

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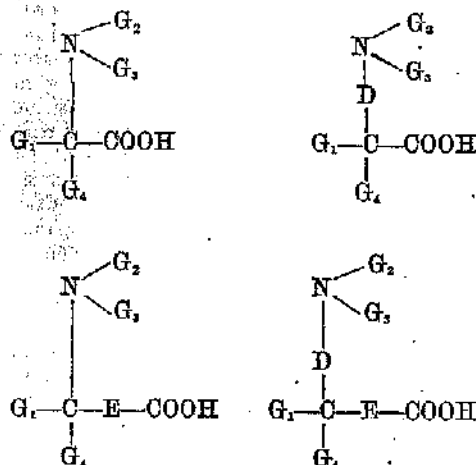
Price 25p

of the said kind may be mentioned for example dihydroxyethyl-ethylene diamine, mono-hydroxymethyl-ethylene triamine, monomethylmonohydroxy-ethyl-
 5 triethylene tetramine, monohydroxyethyl-ethylene diamine, and methylhydroxy-ethyl-ethylene diamine. Substances of the said kind have, with a comparatively low molecular weight, a high basicity
 10 and are therefore especially useful. The invention is not restricted to the use of such comparatively complicated bases, however, but ethylene diamine, for example, may be used itself, but generally speaking it must be used under increased
 15 pressure having regard to its comparatively low boiling point.

A further group of basic substances comprises the alkaline-reacting salts of inorganic bases with inorganic acids. Among these may be mentioned in particular potassium phosphate, potassium metaborate and sodium tetraborate. These substances are usually employed in the form of solutions which contain water as the solvent or as an agent facilitating dissolution. The said substances also dissolve, even if not especially readily, in many organic solvents,
 30 especially those containing hydroxyl groups so that solutions may be employed without any addition of water.

A group intermediate of the two groups already mentioned comprises the salts of strong bases with comparatively weak acids, the bases or the acids or both being organic substances. Among these may be mentioned in particular the alkali or alkaline earth metal salts of weak
 40 organic acids, such as simple or substituted amino acids. For example alanine sodium or potassium salts, glycocoll sodium or potassium salts, methylalanine potassium salt, dimethylalanine sodium salt, dihydroxyethylglycocoll potassium salt and similar substances may be employed with advantage. Salts of amino acids which are derived from amines containing two or more nitrogen atoms frequently
 50 offer special advantages. Amino acids of the said kind may be prepared for example from ethylene diamine or its polymers, in particular diethylene triamine, triethylene tetramine or tetraethylene pentamine. The acids may be derived from these amino compounds in any suitable way. For example suitable carboxylic acids are those which are derived from monobasic acids of the aliphatic series, such as acetic
 60 acid, propionic or butyric acids, or from dibasic or polybasic acids, as for example malonic acid, succinic acid or their homologues, or tricarballic acid, or from monohydroxy or polyhydroxy acids, 65 such as lactic acid, beta-hydroxybutyric

acid, tartaric acid or citric acid, or from keto acids, such as pyruvic acid, or from unsaturated acids, such as maleic acid. Amino acids which already contain a simple or substituted amino group may also serve as initial materials for the acids to be employed. The acids may also be derived from aromatic compounds. In this case they may also contain for example in the ring or in a side chain a
 70 carboxylic group or a sulphonic or other inorganic acid group. The said substances may also be derived from aromatic amines, the amino group being present either in the ring or in a side chain. The acids may also be derived from hydroxy acids, such as salicylic acid, or from halogen acids, such as chlorbenzoic acid. All these substances may also contain
 80 more than one nucleus, such as naphthalene or anthracene. In general the acids may be derived from acyclic, isocyclic or heterocyclic compounds having one or more rings. Acids corresponding to one of the following formulae are especially
 90 suitable:—



(in which:

G_1 and G_2 are hydrogen or hydrocarbon groups which may also contain a hydroxy or a primary, secondary or tertiary amino group or a carboxylic group or more than one of these groups;

G_3 is a hydrocarbon group which may also contain a hydroxy or a primary, secondary or tertiary amino group or a carboxyl group or more than one of these groups;

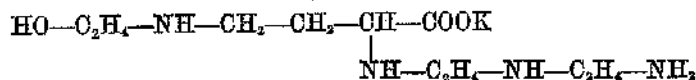
G_4 is hydrogen or an aliphatic hydrocarbon group which may also contain a hydroxy or a primary, secondary or tertiary group or a carboxylic group or more than one of these groups;

D and E are hydrocarbon groups which may also contain a hydroxy or a

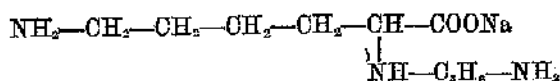
primary, secondary or tertiary amino group or a carboxylic group or more than one of these groups; and in which ring closure may take place in any desired manner between the groups G₁, G₂, G₃, G₄, E and D).

As salts of such acids may be mentioned for example:—

1. gamma - hydroxyethylamino-alpha-diethylenetriamino-butyric acid potassium salt.

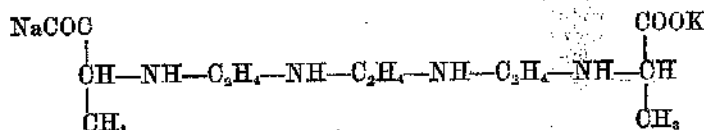


2. alpha - propylenediamino - epsilon-amino caproic acid sodium salt.

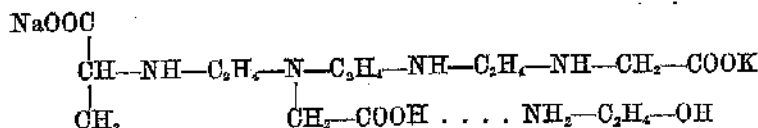


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3. the potassium - sodium salt of alpha.alpha' - (triethylene - tetramino)-dipropionic acid.



4. the potassium-sodium-monoethanolamine salt of triethylene - tetramino-alpha-propionic acid diacetic acid

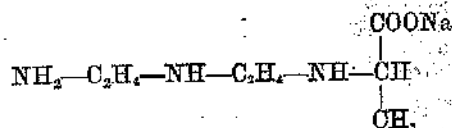


5. the potassium - sodium salt of methylenediamino-diacetic acid

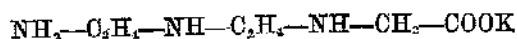


6. the sodium salt of alpha-diethylenetriamino-propionic acid

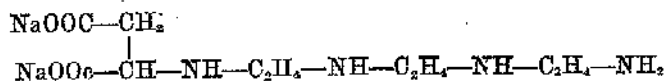
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7. the potassium salt of diethylene-triamino-acetic acid.



8. the sodium salt of triethylenetetramino-succinic acid



9. the potassium salt of methylene-diamino-acetic acid



- $$\text{NH}_2-\text{C}_6\text{H}_4-\text{NH}-\text{CH}_2-\text{COO}-\text{Ba}-\text{OOC}-\text{CH}_2-\text{NH}-\text{C}_6\text{H}_4-\text{NH}_2$$

- $$\text{NH}_2-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}-\underset{\begin{array}{c} | \\ \text{C} \\ | \\ \text{CH}_2-\text{COONa} \end{array}}{\overset{\begin{array}{c} \text{CH}-\text{COO} \\ / \quad \backslash \\ \text{COO} \quad \text{OH} \end{array}}{\text{C}_6\text{H}_5}}$$

- $$\begin{array}{c} \text{KOOC}-\text{CH}-\text{OH} \\ | \\ \text{NaOOC}-\text{CH}-\text{NH}-\text{C}_6\text{H}_4-\text{NH}_2 \end{array}$$

- $$\text{NaOOC}-\text{CH}_2-\text{NH}-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}-\text{CH}_2-\text{COONa}$$

- $$\text{NaOOC}-\text{CH}_2-\text{NH}-\text{C}_2\text{H}_4-\text{N}-\text{C}_2\text{H}_4-\text{NH}-\text{CH}_2-\text{COONa}$$
- $$\quad \quad \quad |$$
- $$\quad \quad \quad \text{CH}_2-\text{COONa}$$

- $$\text{NaOOC}-\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\text{N}}-\text{C}_2\text{H}_5-\text{NH}-\text{CH}_2-\text{COONa}$$

- $$\text{NH}_2-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}-\text{CH}_2-\text{COONa}$$

- $$\begin{array}{c} \text{HO}-\text{CH}-\text{CH}_2-\text{COONa} \\ | \\ \text{NH} \\ | \\ \text{C}_2\text{H}_5-\text{N}-\text{CH}-\text{COOH} \\ | \\ \text{NH}_2 \end{array}$$

- $$\text{NH}_2-\text{C}_2\text{H}_4-\text{NH}-\text{C}_3\text{H}_4-\text{NH}-(\text{CH}_2)_4-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOK}$$

- $$\text{NH}_2-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}-\text{C}_6\text{H}_{10}-\text{COOK}$$

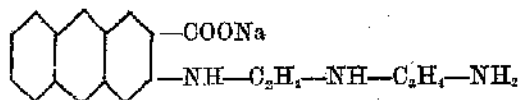
- $$\text{NH}_2-\text{O}_2\text{H}_2-\text{NH}-\text{O}-\text{CH}_3-\text{COOK}$$

- 25

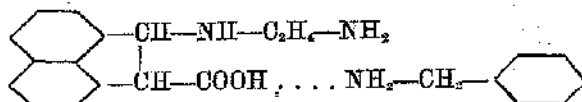
22. the sodium salt of ethylenediamino-beta-methylamino-hydraerylic acid



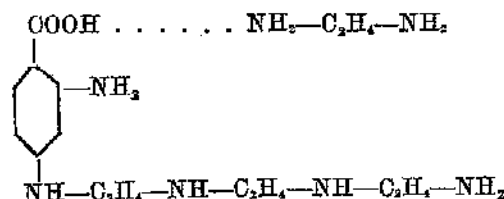
23. the sodium salt of 3-(diethylenetriamino)-anthracene-2-carboxylic acid



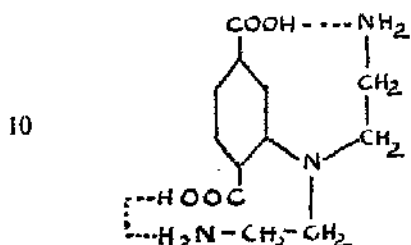
24. the benzylamine salt of ethylenediamino-acenaphthene carboxylic acid



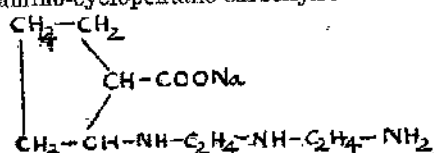
25. the ethylenediamine salt of triethylenetetraminoanthranilic acid



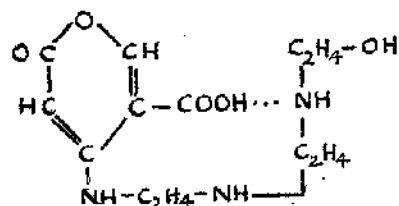
26. diethylenetriamino - terephthalic acid



27. the sodium salt of diethylenetriamino-cyclopentane-carboxylic acid



28. the compound formed by ring closure while splitting off water from the diethanolamine salt of ethylenediamino-cumalic acid



As salts of weak acids with strong

organic bases in this group may be further mentioned for example monoethanolamine borate, ethylenediamine phosphate, ethylenediamine metaborate, the alanine salt of triethylenetetramine and the phenol salt of tetramethylammonium hydroxide.

In many cases it is advantageous to employ basic substances which contain no nitrogen or in which hydrogen atoms are no longer attached to any nitrogen atoms present, because substances of this kind have a longer life in some cases. In such cases, for example potassium metaborate, potassium carbonate, triethanolamine, butyldiethanolamine and dimethyldihydroxyethylethylene diamine or the sodium salt of dimethylalanine, the potassium salt of dihydroxyethylglycocoll or the potassium salt of methylhydroxyethylalanine may be used.

Instead of the single basic substances, mixtures of two or more of such substances may be employed and the single components may belong to different groups among those already mentioned.

The basic substances may either be used as such, provided they are liquid under the reaction conditions, or in the form of their solutions. For example pure triethanolamine may be used as the purifying agent. When solutions of the basic substances are employed, water or any

non-hydrating solvent or any mixture of two or more solvents may be employed. Among non-hydrating solvents, those are particularly suitable which have a good solvent power for the basic substances employed and a high boiling point. As such solvents may be mentioned for example hydrocarbons of high boiling point which may belong to the aromatic, cycloaliphatic or aliphatic series, or mixtures of the same, as for example the usual washing oils, mineral coal tar oils, brown coal tar oils, the oils arising from low temperature carbonisation, cracking and destructive hydrogenation processes, petroleum fractions and tetrahydronaphthalene. Although fractions of comparatively low boiling point of the said hydrocarbon mixtures can be employed, it is usually advantageous not to employ substances having a boiling point of less than 100° Centigrade. Oxygen-containing solvents, such as ethers, ketones and alcohols may also be employed. Especially suitable are for example industrial amyl alcohol and the mixture, consisting mainly of isobutyl alcohol, known as isobutyl oil and arising from the catalytic reduction of the oxides of carbon. Polyhydric alcohols, such as glycol or glycerine, or the numerous substances used in industry as solvents for various purposes may also be employed. By mixing two or more solvents with each other, the boiling point may for example be raised or the solvent power for the basic substances increased or the wetting power of the solution for the gases may be improved. If necessary there may be added to the solutions for the same purpose other solid or semisolid substances, as for example paraffin wax or inorganic salts, or agents which reduce the surface tension, as for example alkylated aromatic sulphonic acids. Such additions need not give true solutions, but may also be employed as emulsions or suspensions. For example a suspension of calcium chloride in amyl alcohol may be employed. Two or more solvents which do not mix with each other may also be employed, the basic substance being dissolved only in one of the solvents while the other promotes the wetting of the gas with liquid. Such a mixture is for example a solution of the sodium salt of alanine in water mixed with amyl alcohol.

The concentration of the basic substances may vary within any desired limits. Thus, as already mentioned, organic bases may be employed in an undiluted state provided they are liquid, as for example triethanolamine. The concentrations which are most favourable depend on the basic substances to be used

and on their properties. In the case of solutions of solid substances, the concentration should in most cases not exceed the concentration of saturation, but in some cases solutions may be used which are saturated at the working temperature or which even then still contain solid basic substances in an undissolved form. Generally speaking the most favourable concentrations of the basic substances lie between 20 and 60 per cent.

Generally speaking it is advantageous to carry out the conversion of the organically combined sulphur in the presence of water. Even very small amounts are, however, sufficient so that even when non-aqueous solutions are employed the small amounts of water which are almost always present in the solutions or in the gases to be purified are sufficient. If necessary, however, the gases may be previously moistened or water may be added to the purifying agent in the form of liquid or vapour.

The process according to this invention is applicable to any gas which contains organically combined sulphur. Water gas, coke-oven gases, producer gas and illuminating gas may be mentioned in particular and also many waste gases, as for example low temperature carbonisation gases or cracking gases. When selecting the reaction temperature it should be borne in mind that the conversion of the organic sulphur compounds proceeds better the higher the temperature. For reasons of economy, however, there are usually used only such high temperatures that the conversion proceeds to the desired extent and with satisfactory speed. Generally speaking therefore temperatures between about 90° and about 150° or 200° Centigrade are usually employed. The reaction temperature may generally speaking be the lower the more strongly basic the substances employed.

The basic substances employed according to this invention have in themselves the property of being capable of absorbing gaseous weak acids, as for example hydrogen sulphide and carbon dioxide and of evolving them again when heated. This invention is not concerned with such an absorption of hydrogen sulphide and at the temperatures employed the basic substances are capable of absorbing only small amounts of gaseous weak acids. When therefore a gas is treated which contains a weak gaseous acid such as hydrogen sulphide or carbon dioxide in addition to organically combined sulphur, there may first occur to a certain extent an absorption of these gaseous weak acids by the purifying agent. After some time, however, a state of equilibrium is set up,

the content of hydrogen sulphide in the gas then not being reduced but even increased by the hydrogen sulphide formed by the conversion of the organically combined sulphur. In spite of this content of gaseous weak acids, the purifying agent acts in the manner already described.

When a content of hydrogen sulphide or other gaseous weak acids in the gas is not undesirable, it is not necessary to remove the hydrogen sulphide formed by the conversion of the organically combined sulphur from the gas. If, on the other hand, it is desired to obtain a gas which no longer contains hydrogen sulphide, the hydrogen sulphide formed may be removed in any suitable manner. For example the gas freed from organically combined sulphur may be led over bog iron ore or similar purifying masses or treated by a wet purification method. When the crude gas contains hydrogen sulphide in addition to organically combined sulphur, the said hydrogen sulphide may either be removed before the conversion of the organically combined sulphur or else together with the hydrogen sulphide formed by the said conversion. When a content of carbon dioxide in the gas is not undesirable, it is advantageous to employ for the removal of hydrogen sulphide after and, if desired, before the conversion of the organically combined sulphur, a method by which no substantial alteration in the content of carbon dioxide in the gas takes place. On the other hand, the removal of the hydrogen sulphide formed after the conversion of the organically combined sulphur also offers the opportunity simultaneously to reduce the carbon dioxide content of the gas.

Any suitable apparatus may be used for the conversion of the organic sulphur compounds. Generally speaking provision should be made for the most intimate possible contact between gas and liquid. This may be effected either by very fine distribution of the liquid purifying agent in the gas by spraying in very fine droplets, as for example by employing nozzles, or by very fine distribution of the gas in the liquid purifying agent. The latter kind of distribution is effected for example by leading in the gas through porous plates or by distributing the gas in the liquid with the aid of a rapidly rotating stirring means. Means lying between the two said extremes may also be employed. For example mechanically moved washers, such as disintegrators, Feld washers or Ströder washers, or stationary washing towers may be employed. The process may be carried out by leading the gas through an amount of

liquid which remains continually in the washing apparatus and which is kept at the desired temperature. The gas may also if necessary be preheated to the working temperature. On the other hand, the purifying agent may also be heated outside the reaction vessel to the reaction temperature and led in a cycle through the purifying apparatus, as for example a washing tower.

The reaction temperature may be maintained in any desired manner as for example by direct heating with combustion gases or by heating by steam coils or the like. Waste gases, the heat content of which cannot otherwise be satisfactorily utilised, are also frequently very useful heating agents because only comparatively low temperatures are necessary. Electric heating may also be employed by reason of the ease with which it may be regulated. If it is desired to make provision for a certain temperature not being exceeded, for example a solvent for the basic substance may be employed the boiling point of which lies at the desired upper limit of temperature and which is kept boiling and thereby partially vaporised, the vapours being condensed in a suitable manner and returned to the solution.

The process may be carried out under any desired pressure. The use of reduced pressure, however, rarely offers advantages. Generally speaking it is most economical to work at the prevailing gas pressure. An increase in the pressure may, however, offer advantages because at pressures above atmospheric pressure the temperature of the liquid purifying agent may be higher without vaporisation taking place. Since the compression of gases causes a considerable evolution of heat, there is the possibility according to this invention of using this heat in order to bring the liquid to the necessary reaction temperature and to keep it at the same. As an example of the desulphurisation of a gas under pressure may be mentioned the treatment of a mixture of water gas and nitrogen serving for the synthesis of ammonia and which has been obtained by the reaction of coke with steam and subsequent mixing of the water gas with nitrogen.

The following Examples will further illustrate the nature of this invention but the invention is not restricted to these Examples.

EXAMPLE 1.

Water gas which has been freed from hydrogen sulphide with the aid of ferric acid gas purifying mass but which still contains 148 milligrams of organically combined sulphur per cubic metre is led

with the aid of a porous plate through a 20 per cent. aqueous solution of triethanol-amine, the liquid being heated to 95° Centigrade in an oil bath. Depending on the height of the liquid, a more or less large amount of organically combined sulphur is converted into hydrogen sulphide. If isoamyl alcohol be employed as the solvent instead of water, the conversion of organically combined sulphur into hydrogen sulphide with the same height of liquid is considerably better even at a higher gas speed.

In a similar manner, a conversion of organically combined sulphur may be carried out at 105° Centigrade by means of a 10 per cent. solution of potassium carbonate in isoamyl alcohol or an aqueous solution of the sodium salt of alanine having a specific gravity at 20° Centigrade of 1.18 or an aqueous solution of the potassium salt of methylalanine having a specific gravity at 20° Centigrade of from 1.18 to 1.25.

EXAMPLE 2.

A washing tower which is well insulated against heat radiation and is indirectly heated at various points with steam is trickled with a hot aqueous 37.8 per cent. solution of the sodium salt of triethylene-tetraminoacetic acid. The temperature in the washing tower and in the solution is kept at about 105° Centigrade. If a water gas from which the hydrogen sulphide has been removed but which still contains 149 milligrams of organically combined sulphur per cubic metre be charged through the tower at a speed of 100 volumes of the washing space per hour, the organically combined sulphur is practically completely converted into hydrogen sulphide.

Dated this 2nd day of July, 1934.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

COMPLETE SPECIFICATION

Improvements in the Removal of Organically Combined Sulphur from Gases

We, COURTIS & COMPANY, a Company with unlimited liability, incorporated under the Companies Act, of 440, Strand, in the County of London, and FREDERICK JOHNSON, a British Subject, of 218, Victoria Drive, Eastbourne, in the County of Sussex, legal representatives of James Yate Johnson, deceased, late of 47, Lincoln's Inn Fields, in the County of London, do hereby declare the nature of this invention (which has been communicated from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfurt-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

It is already known that organically combined sulphur in gases is frequently very troublesome, especially when the gases are to be subjected to catalytic processes.

Among the processes hitherto proposed for the removal of the organically combined sulphur, the catalytic conversion of the organically combined sulphur into hydrogen sulphide has so far proved the most efficient. Catalysts are employed which contain heavy metals, in particular iron, lead, molybdenum, nickel or tungsten, or advantageously molybdenum

or tungsten sulphide. This process has the drawback that comparatively high temperatures of from 300° to 600° Centigrade must be employed.

It has also been proposed to lead the gases at about 200° Centigrade over a metal of the 6th, 6th or 7th group of the periodic system which contains a metal of another group, the exhausted metallic mass being regenerated by treatment with oxygen-containing gases at about 450° Centigrade. This process is comparatively troublesome and expensive.

It has also been proposed for example in specification No. 14569/00, to remove organically combined sulphur from gases by treating them with an amine preferably soluble in alcohol, as for instance with an alcoholic solution of aniline, at low temperatures. Similar processes have also been suggested making use for example of finely divided sulphur impregnated with an amine, especially aniline; or of mixtures of aliphatic or aromatic amines as for example aniline with insoluble metal oxides or metal salts; or of amines, such as aniline, ethylamine and diethylamine together with hydroxides, sulphides or sulphhydrates of the alkali or alkaline earth metals at a temperature as high as circumstances permit (40° Centigrade for example). None of these processes has been commercially success-

ful by reason of the slow rate of reaction with the weak bases employed, and the loss of activity and the great waste of solution owing to absorption of the weak gaseous acids at the low temperatures employed.

It has also been observed in connection with the recovery of weak gaseous acids from gas mixtures containing the same by means of organic bases at low temperatures that the process is not suitable for recovering carbon disulphide from gases, because this reacts with the amines, except tertiary amines, with the formation of derivatives of dithiocarbamic acid or of thiocarbamide.

Our foreign correspondents have now found that organically combined sulphur, such as carbon disulphide and especially carbon oxysulphide, can be removed from gases by bringing the gas to be purified into contact with strong organic bases or basic reacting salts of strong inorganic or organic bases at such high temperatures that the organically combined sulphur is converted into hydrogen sulphide which is led away from the purifying agent together with the gas, and that no substantial absorption of weak gaseous acids by the purifying agent takes place.

The basic substances which may be employed according to this invention are divisible into three groups. The first group comprises the organic bases among which are all strongly basic amines and especially those containing hydroxyl groups. Tetramethylammonium hydroxide, monoethanolamine, diethanolamine, triethanolamine, butyldiethanolamine and dimethylethanolamine may be mentioned by way of example. Still stronger basic amines which contain more than 20 per cent. of nitrogen and more than one nitrogen atom, as for example diamino-isopropanol, may also be employed. The use of bases containing at least two atoms of nitrogen in the molecule and corresponding to the general formula:



(in which B is an aliphatic hydrocarbon radicle which may also contain a simple or substituted amino group and in which at least one of the groups A is an alkyl or aryl group which may contain a hydroxyl group or a simple or substituted amino group, or in which two groups A attached to different nitrogen atoms constitute an alkylene group while each of the remain-

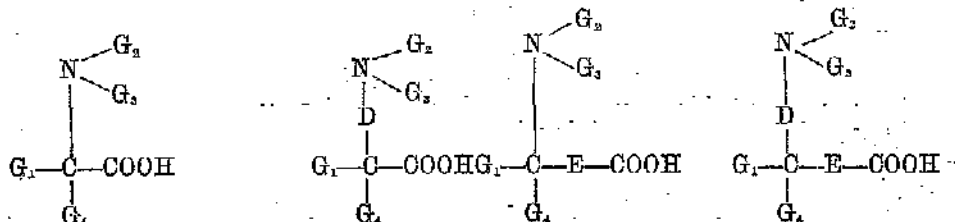
ing groups A is hydrogen or an alkyl or aryl group) offers special advantages. Bases of the said kind are advantageously derived from readily accessible unsaturated hydrocarbons, such as ethylene or propylene. There may be mentioned in particular the substitution products of ethylene diamine, diethylene triamine, triethylene tetramine and tetraethylene pentamine and the corresponding derivatives of triaminopropylene, triaminobutylene and tetraaminobutylene. As suitable substances of the said kind may be mentioned for example dihydroxy-ethylene diamine, monohydroxymethyl-ethylene triamine, monomethylmonohydroxyethyltriethylene tetramine, monohydroxyethyl-ethylene diamine, and methyl-hydroxyethyl-ethylene diamine. Substances of the said kind have, with a comparatively low molecular weight, a high basicity and are therefore especially useful. The invention is not restricted to the use of such comparatively complicated bases, however, but ethylene diamine, for example, may be used itself, but generally speaking it must be used under increased pressure having regard to its comparatively low boiling point.

A further group of basic substances comprises the alkaline-reacting salts of inorganic bases with inorganic acids. Among these may be mentioned in particular potassium phosphate, potassium metaborate and sodium tetraborate. These substances are usually employed in the form of solutions which contain water as the solvent or as an agent facilitating dissolution. The said substances also dissolve, even if not especially readily, in many organic solvents, especially those containing hydroxyl groups so that solutions may be employed without any addition of water.

A group intermediate of the two groups already mentioned comprises the salts of strong bases with comparatively weak acids, the bases or the acids or both being organic substances. Among these may be mentioned in particular the alkali or alkaline earth metal salts of weak organic acids, such as simple or substituted amino acids. For example alanine sodium or potassium salts, glycocoll sodium or potassium salts, methylalanine potassium salt, dimethylalanine sodium salt, dihydroxyethylglycocoll potassium salt and similar substances may be employed with advantage. Salts of amino acids which are derived from amines containing two or more nitrogen atoms frequently offer special advantages. Amino acids of the said kind may be prepared for example from ethylene diamine or its polymers, in particular diethylene triamine, tri-

ethylene tetramine or tetraethylene pent-amine. The acids may be derived from these amino compounds in any suitable way. For example suitable carboxylic acids are those which are derived from monobasic acids of the aliphatic series, such as acetic acid, propionic or butyric acids, or from dibasic or polybasic acids, as for example malonic acid, succinic acid or their homologues, or tricarballic acid, or from monohydroxy or polyhydroxy acids, such as lactic acid, beta-hydroxybutyric acid, tartaric acid or citric acid, or from keto acids, such as pyruvic acid, or from unsaturated acids, such as maleic acid. Amino acids which already contain a simple or substituted amino group may also serve as initial materials for the acids to be

employed. The acids may also be derived from aromatic compounds. In this case they may also contain for example in the ring or in a side chain a carboxylic group or a sulphonic or other inorganic acid group. The said substances may also be derived from aromatic amines, the amino group being present either in the ring or in a side chain. The acids may also be derived from hydroxy acids, such as salicylic acid, or from halogen acids, such as chlorobenzoic acid. All these substances may also contain more than one nucleus, such as naphthalene or anthracene. In general the acids may be derived from acyclic, isocyclic or heterocyclic compounds having one or more rings. Acids corresponding to one of the following formulae are especially suitable:—



40 (in which:

G_1 and G_2 are hydrogen or hydrocarbon groups which may also contain a hydroxy or a primary, secondary or tertiary amino group or a carboxylic group or more than one of these groups;

45 G_3 is a hydrocarbon group which may also contain a hydroxy or a primary, secondary or tertiary amino group or a carboxyl group or more than one of these groups;

50 G_4 is a hydrogen or an aliphatic hydrocarbon group which may also contain a hydroxy or a primary, secondary or tertiary group or a carboxylic group or

more than one of these groups;

D and E are hydrocarbon groups which may also contain a hydroxy or a primary, secondary or tertiary amino group or a carboxylic group or more than one of these groups;

and in which ring closure may take place in any desired manner between the groups G_1 , G_2 , G_3 , G_4 , E and D .)

As salts of such acids may be mentioned for example:—

1. gamma-hydroxyethylamino-alpha-diethylenetriamino-butyric acid potassium salt.



70 obtainable by acetylating gamma-amino-butyric acid, brominating the resulting product, converting the bromination product with diethylenetriamine, saponi-

fying the acetyl group and converting the resulting product with ethylene oxide.

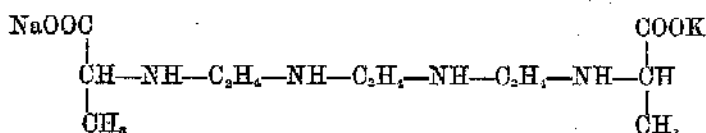
2. alpha-propylenediamino-epsilon-amino caproic acid sodium salt.



80 obtainable by acetylating epsilon-amino caproic acid, brominating the product, converting it with propylene diamine and saponifying the acetyl group.

3. The potassium-sodium salt of alpha-alpha-(triethylene-tetramino)-dipropionic acid

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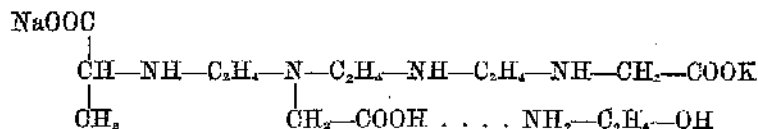


obtainable by reacting triethylenetetramine with two molecular proportions of acetaldehyde and of hydrocyanic acid 5 and saponifying the resulting nitrile by means of a mixture of caustic soda and

caustic potash.

4. the potassium-sodium-monoethanolamine salt of triethylene - tetramino-alpha-propionic acid diacetic acid

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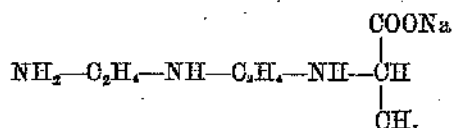


obtainable by converting triethylene-
tetramine with one molecular proportion
of acetaldehyde and of hydrocyanic acid,
15 reacting the resulting product with two
molecular proportions of formaldehyde
and of hydrocyanic acid and saponifying

the resulting product by means of equimolecular proportions of caustic potash, caustic soda and monoethanolamine.

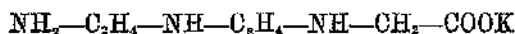
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5. the sodium salt of alpha-diethylene-triamino-propionic acid



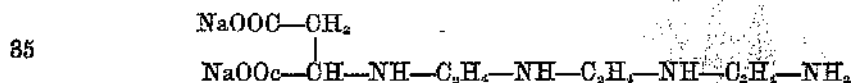
obtainable from diethylenetriamine,
25 acetaldehyde and hydrocyanic acid and
saponification of the resulting product.

6. the potassium salt of diethylene-triamino-acetic acid.



80 obtainable from diethylenetriamine, formaldehyde and hydrocyanic acid and saponification of the resulting product.

7. the sodium salt of triethylene-tetramino-succinic acid



obtainable by reacting alpha-bromo succinic acid with triethylenetetramine.

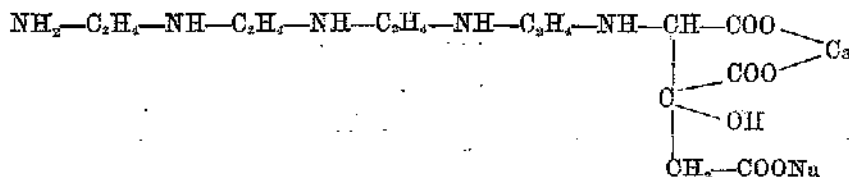
8. the barium salt of ethylenediamino-
acetic acid



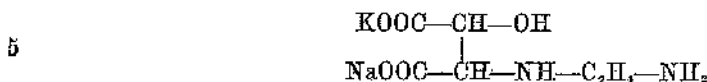
obtainable by reacting ethylenediamine with formaldehyde and hydrocyanic acid and saponifying the resulting nitrile by

means of baryta.

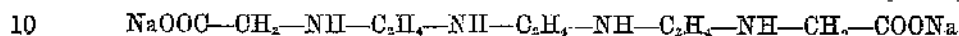
9. The sodium-calcium salt of tetra- 45
ethylenepentamino-citric acid



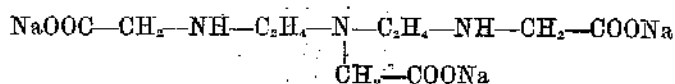
obtainable by reacting tetraethylenepentamine with monobromo-citric acid. 10. the sodium - potassium salt of ethylenediamino-malic acid



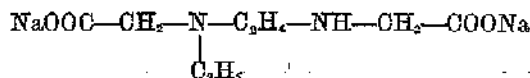
obtainable by converting ethylenediamine with bromo-malic acid. 11. the sodium salt of triethylene-tetramino-diacetic acid



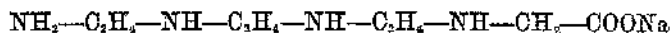
obtainable by reacting triethylene-tetramine with two molecular proportions of formaldehyde and of hydrocyanic acid and saponifying the resulting nitrile. 12. the sodium salt of diethylenetri-amino-triacetic acid 15



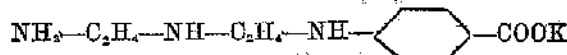
obtainable by reacting diethylenetriamine with three molecular proportions of formaldehyde and of hydrocyanic acid and saponifying the resulting nitrile. 13. the sodium salt of ethyl-ethylene-diamino-diacetic acid



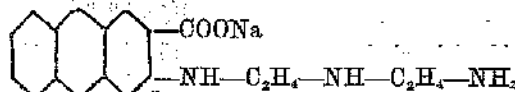
obtainable by reacting ethyl-ethylene-diamine with two molecular proportions of formaldehyde and hydrocyanic acid and saponifying the resulting nitrile. 14. the sodium salt of triethylene-tetramino-acetic acid 30



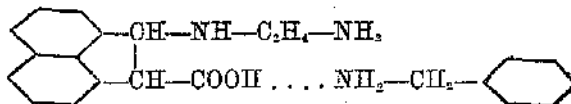
obtainable by reacting triethylene-tetramine with one molecular proportion of formaldehyde and of hydrocyanic acid and saponification of the resulting nitrile. 15. para - diethylenetriamino - benzoic acid potassium salt 35



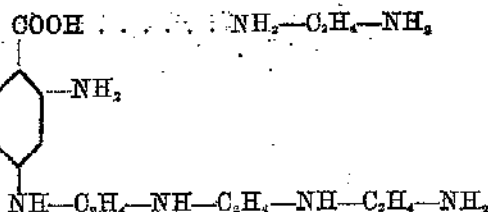
obtainable from diethylenetriamine and para-chlorbenzoic acid. 16. the sodium salt of 3-(diethylene-triamino)-anthracene-2-carboxylic acid 40



obtainable from 3-chlor-anthracene-2-carboxylic acid and diethylene triamine. 17. the benzylamine salt of ethylene-diamino-acenaphthene carboxylic acid: 45

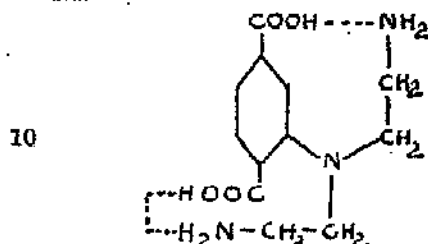


obtainable from chlor-acenaphthene carb-amine. 18. the ethylenediamine salt of tri-oxalic acid and ethylene diamine and neutralising the product with benzyl-ethylenetetramino-anthranilic acid



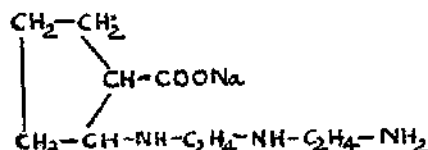
obtainable by acetylating anthranilic acid, chlorinating it and converting the chlorination product with triethylenetetramine, saponifying the acetyl group and neutralising the product with ethylenediamine.

19. diethylenetriamino - terephthalic acid



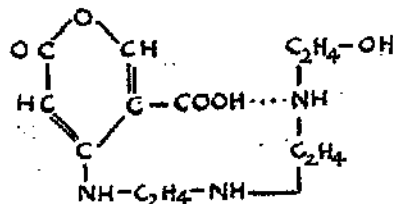
obtainable from diethylene triamine and chlor-terephthalic acid and constituting an intramolecular salt.

20. the sodium salt of diethylenetriamino-cyclopentane carboxylic acid



obtainable from chlor-cyclopentane carboxylic acid and diethylenetriamine.

21. the compound which is obtainable from chlor-cumalic acid and hydroxyethyl-diethylenetriamine and which constitute an intra-molecular salt



As salts of weak acids with strong organic bases in this group may be further mentioned for example monoethanolamine borate, ethylenediamine phosphate,

ethylenediamine metaborate, the alanine salt of triethylenetetramine and the phenol salt of tetramethylammonium hydroxide.

In many cases it is advantageous to employ basic substances which contain no nitrogen or in which hydrogen atoms are no longer attached to any nitrogen atoms present, because substances of this kind have a longer life in some cases. In such cases, for example potassium metaborate, potassium carbonate, triethanolamine, butyldiethanolamine and dimethyldihydroxyethylethylene diamine or the sodium salt of dimethylalanine, the potassium salt of dihydroxyethylglycocoll or the potassium salt of methylhydroxyethylalanine may be used.

Instead of the single basic substances, mixtures of two or more of such substances may be employed and the single components may belong to different groups among those already mentioned.

The basic substances may either be used as such, provided they are liquid under the reaction conditions, or in the form of their solutions. For example pure triethanolamine may be used as the purifying agent. When solutions of the basic substances are employed, water or any non-hydrating solvent or any mixture of two or more solvents may be employed. Among non-hydrating solvents, those are particularly suitable which have a good solvent power for the basic substances employed and a high boiling point. As such solvents may be mentioned for example hydrocarbons of high boiling point which may belong to the aromatic, cycloaliphatic or aliphatic series, or mixtures of the same, as for example the usual washing oils, mineral coal tar oils, brown coal tar oils, the oils arising from low temperature carbonisation, cracking and destructive hydrogenation processes, petroleum fractions and tetrahydronaphthalene. Although fractions of comparatively low boiling point of the said hydrocarbon mixtures can be employed, it is usually advantageous not to employ substances having a boiling point of less than 100° Centigrade. Oxygen-containing solvents, such as ethers, ketones and alcohols may also be employed. Especially

suitable are for example industrial amyl alcohol and the mixture, consisting mainly of isobutyl alcohol, known as isobutyl oil and arising from the catalytic reduction of the oxides of carbon. Polyhydric alcohols, such as glycol or glycerine, or the numerous substances used in industry as solvents for various purposes may also be employed. By mixing two or more solvents with each other, the boiling point may for example be raised or the solvent power for the basic substances increased or the wetting power of the solution for the gases may be improved. If necessary there may be added to the solutions for the same purpose other solid or semisolid substances, as for example paraffin wax or inorganic salts, which do not interfere with the process of the invention, or agents which reduce the surface tension, as for example alkylated aromatic sulphonic acids. Such additions need not give true solutions, but may also be employed as emulsions or suspensions. For example a suspension of calcium chloride in amyl alcohol may be employed as a solvent. Two or more solvents which do not mix with each other may also be employed, the basic substance being dissolved only in one of the solvents while the other promotes the wetting of the gas with liquid. Such a mixture is for example a solution of the sodium salt of alanine in water mixed with amyl alcohol.

The basic substances may also be employed while distributed on solid supports. For example, a porous material, such as lumps of coke, may be soaked with a solution of the basic substance and the gas to be treated passed over the resulting product at the desired temperature.

The concentration of the basic substances may vary within any desired limits. Thus, as already mentioned, organic bases may be employed in an undiluted state provided they are liquid, as for example triethanolamine. The concentrations which are most favourable depend on the basic substances to be used and on their properties. In the case of solutions of solid substances, the concentration should in most cases not exceed the concentration of saturation, but in some cases solutions may be used which are saturated at the working temperature or which even then still contain solid basic substances in an undissolved form. Generally speaking the most favourable concentrations of the basic substances lie between 20 and 60 per cent.

While the process according to this invention may be carried out in the absence of water or moisture it is, generally

speaking, advantageous to carry out the conversion of the organically combined sulphur in the presence of water. Even very small amounts are, however, sufficient so that even when non-aqueous solutions are employed the small amounts of water are almost always present in the solutions or in the gases to be purified are sufficient. If necessary, however, the gases may be previously moistened or water may be added to the purifying agent in the form of liquid or vapour.

The basic substances remain active for a long time. When they are spent, they may for example be regenerated and used for the same purpose or for example for the removal of weak gaseous acids from gases containing the same.

The process according to this invention is applicable to any gas which contains organically combined sulphur. Water gas, coke-oven gases, producer gas and illuminating gas may be mentioned in particular and also many waste gases, as for example low temperature carbonisation gases or cracking gases. When selecting the reaction temperature it should be borne in mind that the conversion of the organic sulphur compounds proceeds better the higher the temperature. For reasons of economy, however, there are usually used only such high temperatures that the conversion proceeds to the desired extent and with satisfactory speed. Generally speaking therefore temperatures between about 90° and about 150° or 200° Centigrade are usually employed. The reaction temperature may generally speaking be the lower the more strongly basic the substances employed.

The basic substances employed according to this invention have in themselves the property of being capable of absorbing gaseous weak acids, as for example hydrogen sulphide and carbon dioxide and of evolving them again when heated. This invention is not concerned with such an absorption of hydrogen sulphide and at the temperatures employed the basic substances are capable of absorbing only small amounts of gaseous weak acids. When therefore a gas is treated which contains a weak gaseous acid such as hydrogen sulphide or carbon dioxide in addition to organically combined sulphur, there may first occur to a certain extent an absorption of these gaseous weak acids by the purifying agent. After some time, however, a state of equilibrium is set up, the content of hydrogen sulphide in the gas then not being reduced but even increased by the hydrogen sulphide formed by the conversion of the organically combined sulphur. In spite of this content of

gaseous weak acids, the purifying agent acts in the manner already described.

When a content of hydrogen sulphide or other gaseous weak acids in the gas is not undesirable, it is not necessary to remove the hydrogen sulphide formed by the conversion of the organically combined sulphur from the gas. If, on the other hand, it is desired to obtain a gas which no longer contains hydrogen sulphide, the hydrogen sulphide formed may be removed in any suitable manner. For example the gas freed from organically combined sulphur may be led over bog iron ore or similar purifying masses or treated by a wet purification method. When the crude gas contains hydrogen sulphide in addition to organically combined sulphur, the said hydrogen sulphide may either be removed before the conversion of the organically combined sulphur or else together with the hydrogen sulphide formed by the said conversion. When a content of carbon dioxide in the gas is not undesirable, it is advantageous to employ for the removal of hydrogen sulphide after and, if desired, before the conversion of the organically combined sulphur, a method by which no substantial alteration in the content of carbon dioxide in the gas takes place. On the other hand, the removal of the hydrogen sulphide formed after the conversion of the organically combined sulphur also offers the opportunity simultaneously to reduce the carbon dioxide content of the gas.

Any suitable apparatus may be used for the conversion of the organic sulphur compounds. Generally speaking provision should be made for the most intimate possible contact between gas and liquid. This may be effected either by very fine distribution of the liquid purifying agent in the gas by spraying in very fine droplets, as for example by employing nozzles, or by very fine distribution of the gas in the liquid purifying agent. The latter kind of distribution is effected for example by leading in the gas through porous plates or by distributing the gas in the liquid with the aid of a rapidly rotating stirring means. Means lying between the two said extremes may also be employed. For example mechanically moved washers, such as disintegrators, Feld washer or Ströder washers, or stationary washing towers may be employed. The process may be carried out by leading the gas through an amount of liquid which remains continually in the washing apparatus and which is kept at the desired temperature. The gas may also if necessary be preheated to the working temperature. On the other hand, the

purifying agent may also be heated outside the reaction vessel to the reaction temperature and led in a cycle through the purifying apparatus, as for example a washing tower.

The reaction temperature may be maintained in any desired manner as for example by direct heating with combustion gases or by heating by steam coils or the like. Waste gases, the heat content of which cannot otherwise be satisfactorily utilised, are also frequently very useful heating agents because only comparatively low temperatures are necessary. Electric heating may also be employed by reason of the ease with which it may be regulated. If it is desired to make provision for a certain temperature not being exceeded, for example a solvent for the basic substance may be employed the boiling point of which lies at the desired upper limit of temperature and which is kept boiling and thereby partially vaporised, the vapours being condensed in a suitable manner and returned to the solution.

The process may be carried out under any desired pressure. The use of reduced pressure, however, rarely offers advantages. Generally speaking it is most economical to work at the prevailing gas pressure. An increase in the pressure may, however, offer advantages because at pressures above atmospheric pressure the temperature of the liquid purifying agent may be higher without vaporisation taking place. Since the compression of gases causes a considerable evolution of heat, there is the possibility according to this invention of using this heat in order to bring the liquid to the necessary reaction temperature and to keep it at the same. As an example of the desulphurisation of a gas under pressure may be mentioned the treatment of a mixture of water gas and nitrogen serving for the synthesis of ammonia and which has been obtained by the reaction of coke with steam and subsequent mixing of the water gas with nitrogen.

The following Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples.

EXAMPLE 1.

Water gas which has been freed from hydrogen sulphide with the aid of ferric oxide gas purifying mass but which still contains 148 milligrams of organically combined sulphur per cubic metre is led with the aid of a porous plate through a 20 per cent. aqueous solution of triethanolamine, the liquid being heated to 95° Centigrade in an oil bath. Depending on the height of the liquid, a more or

less large amount of organically combined sulphur is converted into hydrogen sulphide. If isoamyl alcohol be employed as the solvent instead of water, the conversion of organically combined sulphur into hydrogen sulphide with the same height of liquid is considerably better even at a higher gas speed.

In a similar manner, a conversion of organically combined sulphur may be carried out at 105° Centigrade by means of a 10 per cent. solution of potassium carbonate in isoamyl alcohol or an aqueous solution of the sodium salt of alanine having a specific gravity at 20° Centigrade of 1.18 or an aqueous solution of the potassium salt of methylalanine having a specific gravity at 20° Centigrade of from 1.18 to 1.25.

EXAMPLE 2.

A washing tower which is well insulated against heat radiation and is indirectly heated at various points with steam is trickled with a hot aqueous 37.8 per cent. solution of the sodium salt of triethylenetetramino acetic acid (obtainable from triethylene tetramine and chloroacetic acid). The temperature in the washing tower and in the solution is kept at about 105° Centigrade. If a water gas from which the hydrogen sulphide has been removed but which still contains 149 milligrams of organically combined sulphur per cubic metre be charged through the tower at a speed of 100 volumes of the washing space per hour, the organically combined sulphur is practically completely converted into hydrogen sulphide.

We are aware of specification No. 370,978 according to which carbon oxysulphide is removed from gases by passing the same together with hydrogen at a temperature between 200° and 250° Centigrade over a catalyst consisting of cuprous sulphide and tri-potassium phosphate and potassium carbonate, whereby the carbon oxysulphide is converted into an equivalent quantity of hydrogen sulphide, which is removed by means of any known method. The process according to this

invention differs from the said known process in that no use is made of cuprous sulphide for destroying organically combined sulphur and on the other hand the presence of hydrogen is not necessary. We make no claim to the said known process.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that, subject to the foregoing disclaimer, what we claim is:—

1. A process for the removal of organically combined sulphur from gases which consists in bringing the gas to be purified, preferably in the presence of moisture, into contact with strong organic bases or basic-reacting salts of strong inorganic or organic bases at such high temperatures that the organically combined sulphur is converted into hydrogen sulphide which is led away from the purifying agent together with the gas, and that no substantial absorption of weak gaseous acids by the purifying agent takes place.

2. A specific method of carrying out the process as claimed in claim 1, which consists in employing as strong organic bases such amines as contain one or more hydroxyethyl groups or as contain several nitrogen atoms.

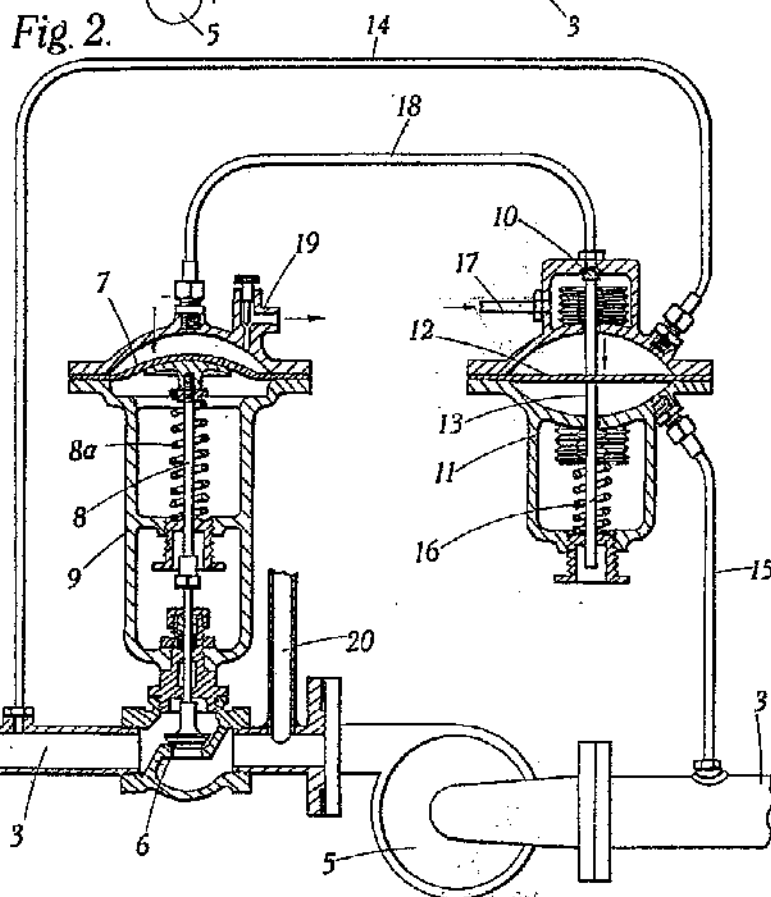
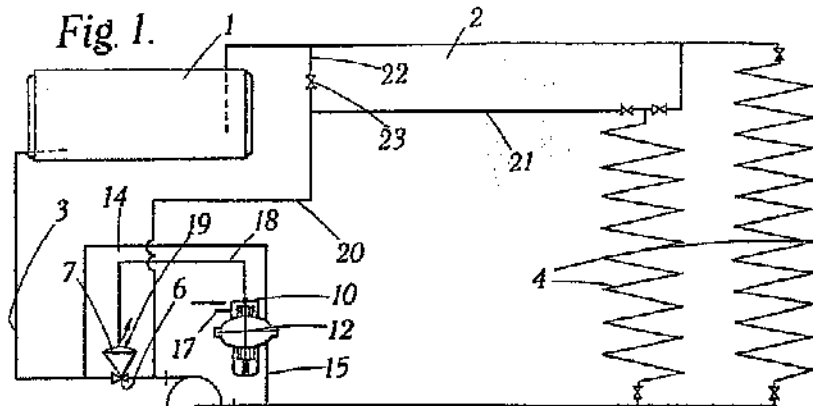
3. A specific method of carrying out the process as claimed in claim 1, which consists in employing as basic-reacting salts such as are derived from simple or substituted amino acids and alkalis or strong organic bases.

4. The process for the removal of organically combined sulphur from gases, substantially as described in each of the foregoing Examples.

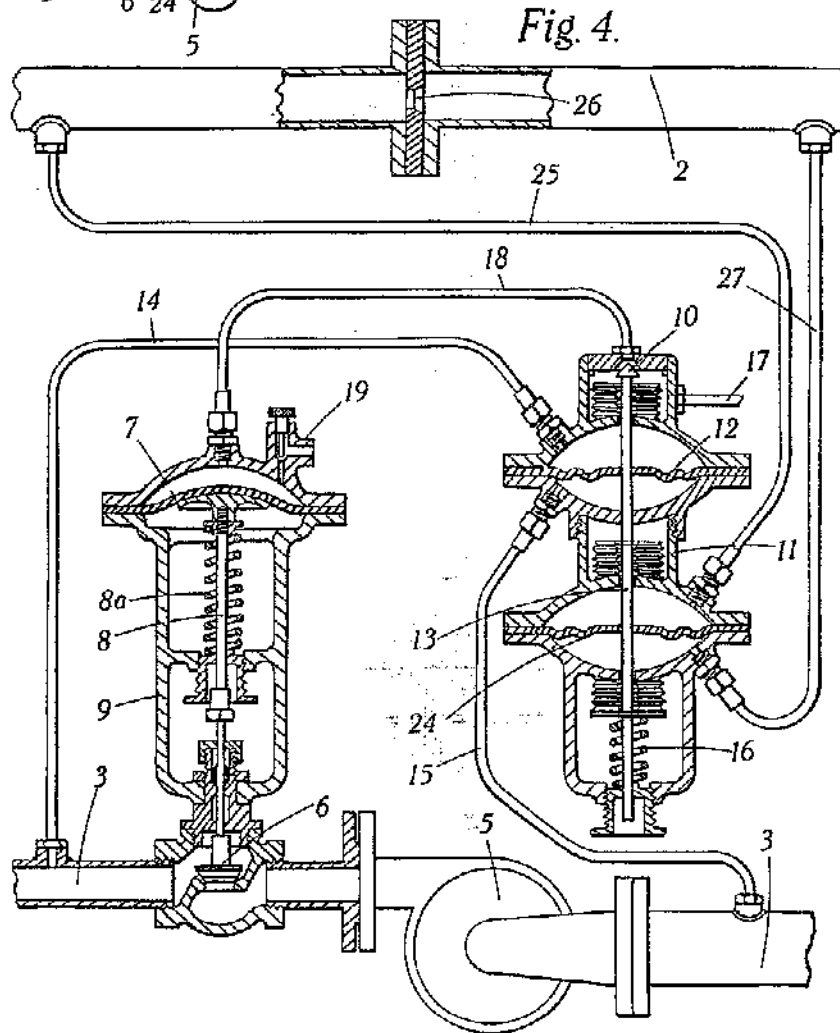
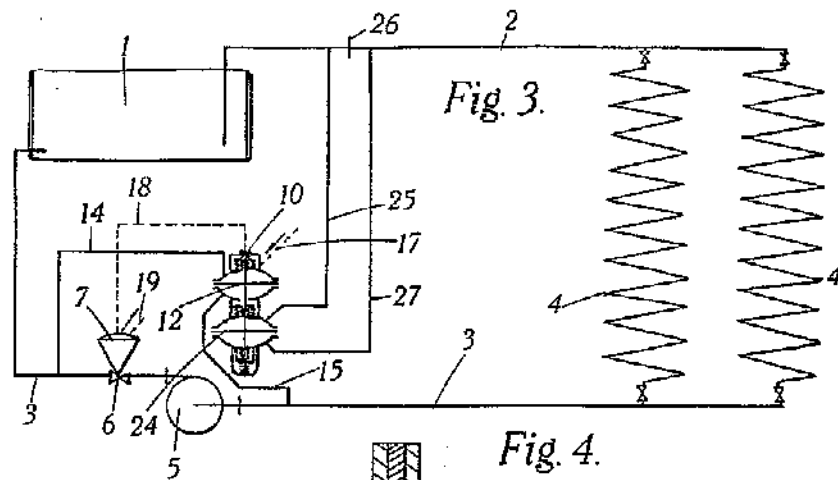
5. Gases when freed from organically combined sulphur by the process particularly described and ascertained or its obvious chemical equivalents.

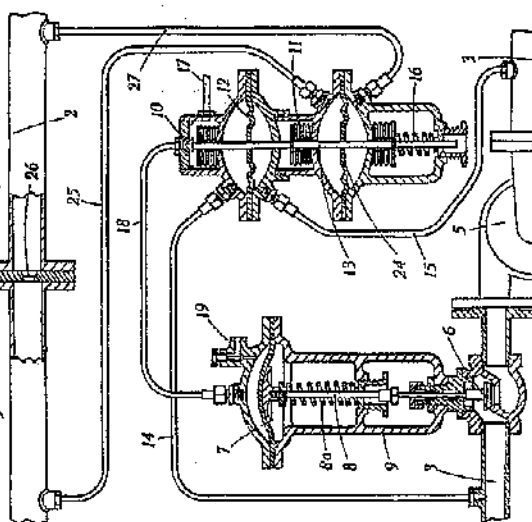
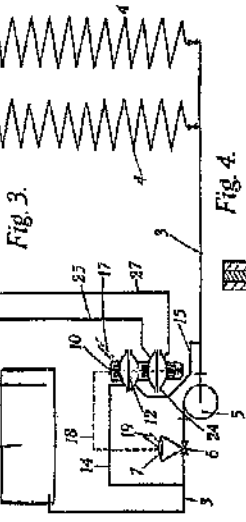
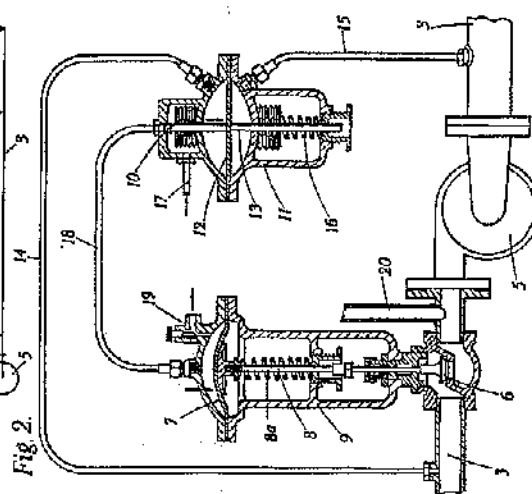
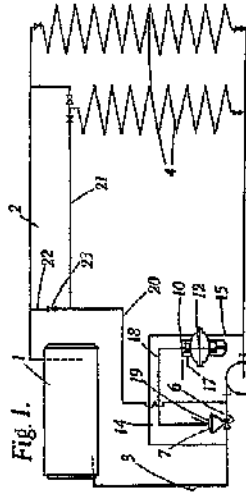
Dated this 10th day of June, 1936.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.



[This Drawing is a reproduction of the Original on a reduced scale.]





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