PATENT SPECIFICATION

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869,127

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COMPLETE SPECIFICATION

DRAWINGS ATTACHED

Process for the Removal of Hydrogen Sulphide from Gases

We, THE GAS COUNCIL, a British Body Corporate, of 1 Grosvenor Place, London S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is for a process for the removal of hydrogen sulphide from gases. Processes employing neutral or acid solutions of zinc sulphate have previously been proposed for the simultaneous removal of hydrogen sulphide and ammonia from gases and have involved the production of ammonium sulphate.

Our co-pending Patent Application No. 9694/56 (812,428), describes and claims the simultaneous purification of gases with ammonia fixation and removal of hydrogen cyanide and employs zinc originally in the form of zinc sulphate. The wash-liquors were weakly ammoniacal such that they contained sufficient ammonium sulphate to prevent the precipitation of zinc as hydroxide or carbonate. The ammonia partial pressures in equilibrium with the wash-liquors were normally of the order of 10 to 20 grains ammonia per 100 standard cu.ft. of gas. In contrast to this and other known methods of gas purification, the process of the present invention removes hydrogen sulphide from gases, and hydrogen cyanide also if present, by the employment of wash-liquors containing zinc in relatively much more strongly ammoniacal solutions, and does not involve the simultaneous removal of ammonia from the gas or the production of ammonium sulphate.

According to the present invention there is provided a process for the purification of gas by the removal of hydrogen sulphide and simultaneously of hydrogen cyanide if present, which process comprises washing the gas with an ammoniacal wash-liquor containing zinc compounds, the ammonia partial pressure in equilibrium with the liquor being such as to provide an ammonia concentration in the gas of not less than 50 grains ammonia per 100 standard cu.ft. of gas, and separating the precipitated zinc compounds from the liquor.

The invention may be applied to the purification of fuel gases containing ammonia, such as cooled, de-tarred coal gas having ammonia concentrations typically in the range 150 to 500 grains ammonia per 100 standard cu.ft. of gas.

Thus, in the purification of such a coal gas containing its normal full content of ammonia, and all or part of its full content of hydrogen sulphide and of hydrogen cyanide, the liquors containing zinc compounds are recirculated or otherwise maintained in contact with the gas so that they are substantially in equilibrium with the concentrations of ammonia and of carbon dioxide present. The ammonia in the liquor is thus extensively carbonated but the relatively high equilibrium partial pressure of ammonia remains and there is no significant net removal of ammonia from the gas.

The zinc content of the wash-liquor which is available for reaction with hydrogen sulphide and hydrogen cyanide, *i.e.* the reactive zinc, is preferably all in solution, mainly in the form of ammines. The precipitated zinc sulphide and zinc cyanide formed during the gas purifying process may be removed by filtration without removing any substantial quantity of unused zinc.

The zinc used in the preparation of the original wash-liquor and for the replenishment of the wash liquor may be in the form of solid zinc oxide, hydroxide or carbonate or any mixture of these compounds, for example the basic carbonate or a partly

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Price 4s 6d

dehydrated hydroxide. These compounds are completely or partially brought into solution by the ammonia present.

A concentration of zinc approaching 10 grams zinc per litre may be retained in solution. One preferred method of maintaining the concentration of zinc is by passing a part or the whole of the used wash-liquor first through a filter or settler for the removal of insoluble zinc compounds formed by reaction of the wash-liquor with hydrogen sulphide and hydrogen cyanide and then bringing the clear liquor into intimate contact with excess of solid zinc oxide, hydroxide or carbonate to raise the concentration of dissolved zinc to approaching saturation value and then separating the excess of solid zinc oxide, hydroxide or carbonate.

The wash-liquor has no significant equilibrium partial pressure of hydrogen sulphide. The process is therefore particularly suitable for completing the removal of hydrogen sulphide from gases, for example to below the statutory limit for town gas. It affords a method for the purification of coal gas before it is washed for ammonia recovery so that the ammonia product is free from hydrogen sulphide and has a relatively low content of hydrogen cyanide.

The rate of absorption of hydrogen sulphide by the ammoniacal zinc solutions is relatively fast, and, when employing a washer in the form of a tower packed with grids of boards on edge irrigated with the ammoniacal zinc solution and with a gas velocity of 7 feet per second between the boards, the height of a given packing required for a given purification duty does not exceed twice that required when employing once-run caustic soda solution containing sodium zincate, with which reagent the rate of absorption of hydrogen sulphide is subject to negligible resistance in the liquid phase so that the required height of packing is a minimum, determined solely by the resistance in the gas phase.

The flow of the wash-liquor with respect to the gas flow may be countercurrent, concurrent or fully mixed. Alternatively there may be continuous recirculation of the liquor. In a preferred application of the present invention employing the available zinc all in solution, the whole of the purification of the gas may be effected in a single washing stage with substantially 100 per cent utilisation of the available zinc by conversion to sulphide or cyanide.

When the present invention is applied to the removal of hydrogen sulphide from gas in relatively small quantities it is economically practical to reject the precipitated zinc compounds.

When large quantities of hydrogen sulphide have to be removed from the gas, the zinc compounds precipitated may after separation be dried and roasted to zinc oxide, for example in a fluidised bed roaster, and the zinc oxide from the roaster used again to replenish the zinc content of the wash-liquor, preferably by a method which ensures that no undissolved zinc oxide passes into the washer. By use of this sequence of operations the process becomes fully regenerative with respect to the zinc employed. The sulphur product of this method of application comprises roaster gases containing oxides of sulphur which may be further treated for example by conversion to sulphuric acid by the contact process.

Because the present invention is suitable for the removal of hydrogen sulphide from coal gas containing ammonia, it may be applied in combination with absorption-desorption processes of liquid purification in which ammonia is employed for the separation of a major part of the hydrogen sulphide as a concentrate of acid gases. Liquor recirculation processes are the simplest methods of partial purification by means of ammonia: the wash liquor is maintained in a closed circuit being first used for countercurrent selective quick washing of unpurified coal gas upstream of the ammonia washers, then reactivated in a deacidifier by stripping with steam to separate the acid gases, and then recooled for re-use in the washer; the ammonia content of the liquor is substantially in equilibrium with that in the coal gas so that there is no significant net absorption of ammonia in the washer. The hydrogen sulphide remaining in the coal gas after such a method of partial purification may be removed completely in a secondary washer by the process of the present invention.

More extensive primary purification by means of ammonia can be effected in a more complex process involving the recirculation of ammonia gas. Hydrogen sulphide removal in this way is limited to about 98% because the ammonia gas available for recirculation is not free from hydrogen sulphide which is the essential condition for the attainment of complete purification. The process of the present invention may be applied directly to such recirculated ammonia gases or by indirect means to secure their freedom from hydrogen sulphide so that complete purification of coal gas is attainable.

Following is a description by way of example and with reference to the diagrammatic drawing accompanying the provisional specification of one method of applying the present invention to the complete purification of coal gas by an absorption-desorption process employing ammoniacal wash liquor and ammonia gas recirculation, the ammoniacal zinc reagent being employed as a guard purifier in such a way that no hydrogen sulphide can enter the ammonia washers and thus be present in the recirculated ammonia gas.

Referring to the drawing, the primary purifier A may consist of a selective quick washer of the bubble-plate type. Cooled and de-tarred unpurified coal gas is passed into this purifier and ammonia gas is fed into the coal gas under all of the bubble plates. This ammonia gas is derived from the distillation, after de-acidification, of the liquor leaving the primary purifier. Irrigation of this selective washer is with ammonia-rich liquor of low hydrogen-sulphide content from the base of the secondary purifier B. The secondary purifier is similar in construction to the primary purifier and is irrigated with liquor of fairly low ammonia content and fed between stages with ammonia gas, both the liquor and the ammonia gas being free from hydrogen sulphide and derived by distillation from the same clean ammonia liquor.

The guard purifier C which follows the secondary purifier is irrigated, in a closed circuit, with an ammoniacal zinc solution in accordance with the present invention. This solution removes any hydrogen sulphide remaining in the gas so that none passes into the ammonia washer D. The mean hydrogen-sulphide removal load and the consequent zinc consumption are inconsiderable. There is no ammonia removal in this washer.

For removing ammonia from the purified gas down to below about 2 grains per 100 cu.ft. a further washer D is provided. It is shown as a selective quick washer irrigated with fresh water and effecting the duty with minimum carbonation of the ammonia.

Ammoniacal liquor free from hydrogen sulphide is received from washer D into the clean ammonia still E. The distillation with live steam yields ammonia gas and stripped liquor, which are used in the secondary purification. The still also produces concentrated liquor of high quality, this being ammonia not recirculated, and thus substantially equivalent in quantity to the ammonia in the gas entering the primary purifier A.

Liquor from the purification stages is stripped in G with live steam to remove acid gases containing hydrogen sulphide substantially equivalent in quantity to that in the untreated coal gas, together with most of the hydrogen cyanide and some carbon dioxide.

De-acidified liquor containing some hydrogen sulphide is distilled with live steam in the still F to produce the ammonia gas required for addition to the primary purifier A. The effluent contains substantially no free ammonia and is equivalent to the fresh water and live steam added to the system.

By this process the coal gas is purified completely to within the statutory limit for hydrogen sulphide concentration in town's gas and all of the hydrogen sulphide is separated as a concentrate of acid gases which may readily be used to make sulphur or sulphuric acid.

Many variations of the system shown in the drawing are possible. Thus, for example, the primary purifier with the de-acidifier and the foul ammonia still might be replaced by a liquor recirculation plant thus reducing the number of steam distillation units.

WHAT WE CLAIM IS:—

1. A process for the purification of gas by the removal of hydrogen sulphide and simultaneously of hydrogen cyanide if present, which process comprises washing the gas with an ammoniacal wash liquor containing zinc compounds, the ammonia partial pressure in equilibrium with the liquor being such as to provide an ammonia concentration in the gas of not less than 50 grains ammonia per 100 standard cubic feet of gas, and separating the precipitated zinc compounds from the liquor.

2. A process as claimed in claim 1 wherein the gas is cooled, de-tarred coal gas.

3. A process as claimed in claim 2 wherein the ammonia concentration in the gas is in the range 150 to 500 grains of ammonia per 100 standard cubic feet of gas.

4. A process as claimed in any one of the preceding claims wherein the wash liquors are maintained in contact with the gas so that they are substantially in equilibrium with the concentrations of ammonia and of carbon dioxide present.

5. A process as claimed in any one of the preceding claims wherein all the reactive zinc present in the wash liquor is in solution.

6. A process as claimed in claim 5 wherein the zinc in solution is mainly in the form of ammines.

7. A process as claimed in any one of the preceding claims which comprises passing the used wash liquor or a part thereof through a filter or settler to remove insoluble zinc compounds and then bringing the clear liquor into intimate contact with excess of solid zinc oxide, hydroxide or carbonate to raise the concentration of dissolved zinc to approach saturation value and then separating the excess of solid zinc oxide, hydroxide or carbonate.

8. A process as claimed in any one of the preceding claims wherein the flow of wash liquor with respect to the gas flow is countercurrent.

9. A process as claimed in any one of the preceding claims wherein the whole of the purification of the gas is effected in a single washing stage with substantially 100 per cent utilisation of the available zinc.

10. A process as claimed in any one of the preceding claims wherein the precipitated zinc compounds are dried and roasted to zinc oxide and the zinc oxide returned to the wash liquor.

11. A process as claimed in claim 10 wherein the zinc compounds are roasted in a fluidised bed roaster.

12. A process for the purification of coal gas substantially as described in the specific example and with reference to the accompanying drawing.

13. Fuel gases when treated by the process claimed in any one of the preceding claims.

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PROVISIONAL SPECIFICATION

Process for the Removal of Hydrogen Sulphide from Gases

We, THE GAS COUNCIL, a British Body Corporate, of 1, Grosvenor Place, London, S.W.1., do hereby declare this invention to be described in the following statement:—

This invention is for a process for the removal of hydrogen sulphide from gases. Processes employing neutral or acid solutions of zinc sulphate have previously been proposed for the simultaneous removal of hydrogen sulphide and ammonia from gases and have involved the production of ammonium sulphate.

Our copending Patent Application No. 9694/56 (Serial No. 812,428) describes the simultaneous purification of gases with ammonia fixation and removal of hydrogen cyanide and employs zinc originally in the form of zinc sulphate. The wash-liquors which were weakly ammoniacal contain sufficient ammonium sulphate to prevent the precipitation of zinc as hydroxide or carbonate. The ammonia partial pressures in equilibrium with the wash-liquors were normally of the order of 10 to 20 grains ammonia per 100 standard cu.ft. of gas. In contrast to this and other known methods of gas purification, the process of the present invention removes hydrogen sulphide from gases, and hydrogen cyanide also if present, by the employment of wash-liquors containing zinc in relatively much more strongly ammoniacal solutions, and does not involve the simultaneous removal of ammonia from the gas or the production of ammonium sulphate.

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The invention may be applied to the purification of cooled, de-tarred coal gas having ammonia concentrations typically in the range 150 to 500 grains ammonia per 100 standard cu.ft. of gas.

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The zinc content of the wash-liquor which is available for reaction with hydrogen sulphide and hydrogen cyanide is preferably all in solution, mainly in the form of ammines. The precipitated zinc sulphide and zinc cyanide formed during the gas purifying process may be removed by filtration without removing any substantial quantity of unused zinc.

The zinc used in the preparation of the original wash-liquor and for the replenishment of the original concentration of zinc may be in the form of solid zinc oxide, hydroxide or carbonate or any mixture of these compounds such for example as the basic carbonate or a partly dehydrated hydroxide. These compounds are completely or partially brought into solution by the ammonia present.

A concentration of zinc approaching 10 grams zinc per litre may be retained in solution. One preferred method of maintaining the concentration of zinc is by passing a part or the whole of the used wash-liquor first through a filter for the removal of insoluble zinc compounds formed by reaction of the wash-liquor with hydrogen sulphide and hydrogen cyanide and then bringing the filtrate into intimate contact with excess of solid zinc oxide, hydroxide or carbonate to raise the concentration of dissolved zinc to approaching saturation value and then separating the excess of solid zinc oxide, hydroxide or carbonate.

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The rate of absorption of hydrogen sulphide by the ammoniacal zinc solutions is relatively fast and when employing a washer in the form of a tower packed with grids of boards on edge irrigated with the ammoniacal zinc solution and with a standard gas velocity of 7 feet per second between the boards, the height of a given packing required for a given purification duty does not exceed twice that required when employing once-run caustic soda solution containing sodium zincate with which reagent the rate of absorption of hydrogen sulphide is subject to negligible resistance in the liquid phase so that the required height of packing is a minimum determined solely by the resistance in the gas phase.

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The guard purifier which follows the secondary purifier is irrigated, in a closed circuit, with an ammoniacal zinc solution in accordance with the present invention. This solution removes any hydrogen sulphide remaining in the gas so that none passes into the ammonia washer C. The mean hydrogen-sulphide removal load and the consequent zinc consumption are inconsiderable. There is no ammonia removal in this washer.

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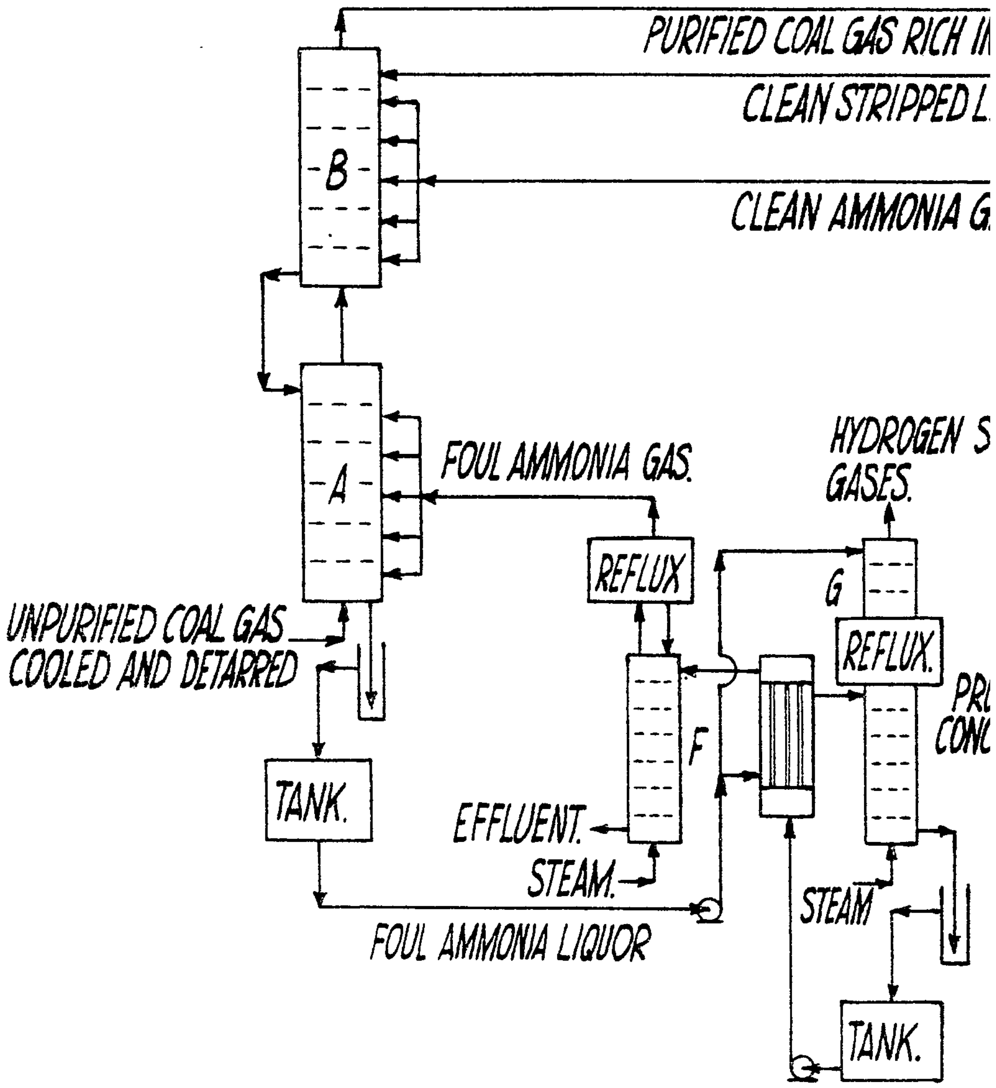
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869,127 PROVISIONAL SPECIFICATION

1 SHEET

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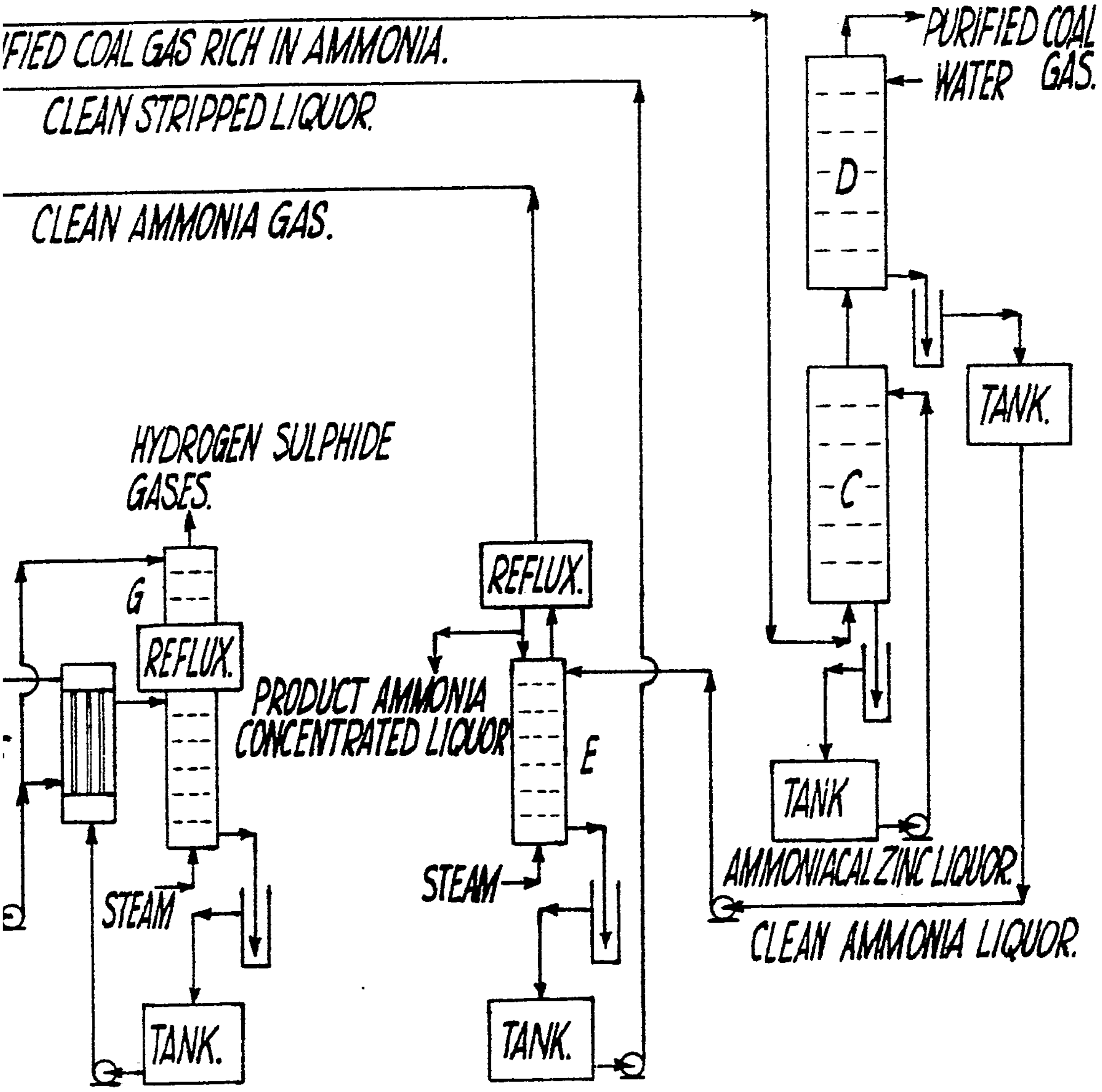

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