

PATENT SPECIFICATION

Inventors: JOHN DAVID FRANCIS MARSH and WILLIAM BARRY SAVILE NEWLING

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COMPLETE SPECIFICATION

Improvements in or relating to the Purification of 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 improvements in or relating to the purification of gases and is particularly concerned with the purification of fuel gases, e.g. coal gas or coke-oven gas, from which both hydrogen sulphide and hydrogen cyanide must be removed. The invention is particularly applicable to gases which also contain ammonia that must be removed.

It is an object of the present invention to reduce the hydrogen sulphide concentration in a fuel gas to a very low level, for example below the statutory limit for town gas, approximately 0.7 parts per million by volume.

A further object of the present invention is to reduce the hydrogen cyanide concentration in a fuel gas to a low level, for example, below 5 grains per 100 cu.ft.

There have been a number of known processes for the removal of hydrogen sulphide from gases by the use of zinc sulphate solution. These processes were all characterised by a purification stage which may be represented as:—

$2\text{NH}_3 + \text{ZnSO}_4 + \text{H}_2\text{S} = \text{ZnS} + (\text{NH}_4)_2\text{SO}_4$, by the separation of the zinc sulphide precipitate, and by the reversion of this sulphide to zinc sulphate for re-use in the process. Emphasis was laid upon the complete removal of ammonia from the gas and its recovery as pure ammonium sulphate. The regenerated zinc sulphate solutions in most of these processes tended to be acid.

There is no disclosure in the known art of the use of zinc sulphate solution for the substantially complete removal of hydrogen sulphide from a gas with full regeneration and re-use of the zinc sulphate reagent, the emphasis being on conditions which are unsuitable for complete purification. One condition for

complete purification is that the zinc sulphate solution should be alkaline. However, the presence of alkali is objectionable for the following two reasons: (a) the zinc ions tend to be removed from solution as precipitated zinc hydroxide or carbonate and are thereby made ineffective for the removal of hydrogen sulphide and (b) the zinc ions tend to react with any hydrogen cyanide present to form soluble compound ions which are not effective for complete hydrogen sulphide removal and which may make it very difficult to operate the process to obtain an ammonium sulphate product that is free from zinc.

A well-known method for the analysis of gases for hydrogen sulphide and hydrogen cyanide concentration employs strongly ammoniacal zinc sulphate solution in such manner that these two components are completely removed from the gas and remain with the reagent respectively as precipitated zinc sulphide and soluble ammonium zincicyanide.

This and further known properties of the cyanogen compounds of zinc would lead those skilled in the art to predict that the known processes could not readily be applied to a gas containing hydrogen cyanide to produce ammonium sulphate free from soluble zinc compounds.

To secure a substantial removal of hydrogen cyanide by a continuous process with full regeneration and re-use of the zinc sulphate reagent it is necessary to establish conditions in which an insoluble cyanogen compound is formed; this can then be separated and subjected to a chemical treatment to regenerate the reagent quantitatively.

The equilibria in ammoniacal solutions of zinc sulphate used for the absorption of hydrogen cyanide are represented by equilibrium constants published in the literature. No calculation from these known constants predicts the formation of an insoluble cyanogen compound of zinc under any conditions likely to be useful in a continuous process for the removal of hydrogen cyanide from gas with

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full regeneration and re-use of the zinc sulphate reagent.

5 In contrast to this prediction from the known constants we have found by experiment that if weakly ammoniacal zinc sulphate is used to remove hydrogen sulphide from gas containing also hydrogen cyanide, the precipitation of cyanogen compounds of zinc is very considerable indeed. This phenomenon is associated with the simultaneous precipitation of zinc sulphide and would not otherwise occur. The sulphide precipitate is known to occlude much foreign matter, but the co-precipitation of cyanogen compounds is quite exceptional.

10 If small quantities of ammonia are added to neutral zinc sulphate solution, zinc hydroxide is precipitated. If more ammonia is added, the zinc hydroxide redissolves, most of the zinc in solution being combined with ammonia as ions of the amine type. In a solution containing about 3% ZnSO_4 by weight the precipitation of zinc hydroxide is prevented by the addition of enough ammonia to raise the pH above 10. If a substantial concentration of ammonium sulphate is present the pH may be much lower without the precipitation of zinc hydroxide. Such liquors, if very rich in ammonium sulphate, may be free from insoluble zinc hydroxide and have a low ammonia vapour pressure, for example, less than 5 grains NH_3 per 100 cu.ft. at 20°C .

20 The weakly ammoniacal zinc sulphate solutions employed in the process of the present invention are such that they contain sufficient ammonium sulphate to prevent the precipitation of zinc hydroxide. The free ammonia content is however sufficiently low to permit them to be employed in the process so that the resulting purified gas contains not more than 50 grains NH_3 per 100 cu.ft. and preferably not more than 20 grains.

25 The concentration of salts present is preferably high but not so high that the separation of crystals of zinc ammonium sulphate becomes possible.

30 According to the present invention there is provided a process for the simultaneous removal of hydrogen sulphide and hydrogen cyanide from fuel gas which process comprises washing the gas with a weakly ammoniacal zinc sulphate solution containing sufficient ammonium sulphate to prevent the precipitation of zinc hydroxide, separating the precipitated zinc sulphide and insoluble cyanogen compounds of zinc from the resultant solution, processing the said solution for the recovery of crystalline ammonium sulphate substantially free from zinc compounds, and reconverting said precipitate to zinc sulphate for re-use in the process.

35 The process is particularly suitable for the treatment of coal gas and coke-oven gas and is preferably applied to such gases so that the greater part of their ammonia content is

removed simultaneously with the hydrogen sulphide and hydrogen cyanide.

The process of the present invention consumes ammonia equivalent to the hydrogen sulphide and hydrogen cyanide removed; a further quantity of ammonia may be needed to bring the regenerated zinc sulphate solution to the necessary ammoniacal condition. Where insufficient ammonia is present in the gas to be treated, additional quantities may be added to the system, for example, directly to the zinc sulphate solution as concentrated ammoniacal liquor.

40 In one preferred application of the present invention coal-gas or coke-oven gas to be purified is washed in a primary purification process with an ammoniacal solution for the removal of the major proportion, e.g. 80%, of the hydrogen sulphide present in such manner that little change is effected in the ammonia concentration in the gas which is accordingly more than the equivalent of the hydrogen sulphide and hydrogen cyanide in the gas. The present process is then applied for secondary purification of the gas to remove all the remaining hydrogen sulphide and most of the hydrogen cyanide and ammonia.

45 In one preferred method of washing the gas the greater part of the wash liquor is continuously recirculated so that the change in the composition of the wash liquor on one passage through the washer is relatively small. With this system by removing the greater part of the precipitate, present after one passage of the liquor through the washer, before returning the liquor to the washer it is possible to combine a high concentration of ammonium sulphate in the wash liquor with a low content of precipitate in the washer; the concentration of ammonium sulphate also becomes large in relation to the concentration of unfixed ammonia present with it in the liquor. Conditions resulting from the recirculation method are therefore favourable for maintaining the desired high proportion of ammonium sulphate and for the processing of the excess volume of liquid for the production of crystalline ammonium sulphate. The recirculated wash liquor after substantial reduction of its content of precipitate but before returning to the washer may be mixed with regenerated zinc sulphate solution and ammoniacal liquids so that the liquid entering the washer does not vary greatly in composition.

50 The ammonium sulphate may be recovered from the wash liquor after the separation of the precipitated zinc sulphide and insoluble cyanogen compounds of zinc by treating the wash liquor to convert all the zinc remaining in solution to insoluble zinc sulphide, filtering to separate the zinc sulphide and thereafter stripping the filtrate with steam to remove volatile impurities and converting the ammonium sulphate solution to the crystalline salt in an evaporative crystalliser.

To effect this final precipitation of soluble zinc the wash liquor may be treated with hydrogen sulphide, ammonium sulphide or ammonium hydrosulphide. The sulphiding agent may contain hydrogen cyanide, but this must be in low absolute concentration; thus the hydrogen sulphide gases produced in the process when using the acid method for regeneration of the zinc sulphate reagent is unsuitable because of the high partial pressure of hydrogen cyanide present. Suitable reagents include concentrated ammoniacal liquor which is rich in dissolved hydrogen sulphide, unpurified coal gas or coke-oven gas, or similar gases from which the major proportion of hydrogen sulphide, e.g. 80%, has been removed by washing with aqueous ammonia.

It is preferable that the wash liquor sulphided in this manner should be initially free from precipitate containing cyanogen compounds of zinc, but if such precipitate is present the sulphiding treatment is likely to convert the insoluble cyanogen compounds to zinc sulphide.

It is important that the quantity of zinc precipitated as sulphide in processing the wash liquor for ammonium sulphate recovery should be small in proportion to that separated from the wash liquor used in the main washing stage. The removal of the precipitate from the main washing stage is the only substantial purge of cyanogen compounds from the washing system. Thus the continued removal of hydrogen cyanide from the gas is dependent upon the separation of this precipitate.

For the regeneration of zinc sulphate from the wash liquor two methods are available. The precipitate may be washed to reduce its content of ammonium sulphate and thereafter fed to a roaster, preferably as a slurry, and roasted in a fluidised bed with sulphur or hydrogen sulphide equivalent to the cyanogen

compounds of zinc present and to the excess of sulphur required to ensure substantially complete conversion of all the zinc to zinc sulphate. Alternatively, the zinc sulphate may be obtained from the precipitate separated from the wash liquor by dissolving the precipitate in sulphuric acid, at least two equivalents of acid being necessary for each equivalent of zinc.

The gas after removal of hydrogen sulphide and hydrogen cyanide therefrom may be subjected to a final wash employing water, sulphuric acid or regenerated zinc sulphate solution in order to remove any residual ammonia in the gas. The used washing medium may be mixed with liquid recirculated in the main washing stage.

Heat is generated by the chemical reactions involved in the process; means for removing this heat may be desirable. A preferred method is to allow the heat to be carried forward in the gas as sensible heat and as the latent heat of water of saturation; the cooling may then be effected in a condenser and the aqueous condensate returned to the process to the extent and to the places which will give the best control of the water balance of the process and of the concentration levels of the aqueous solutions employed.

Following is a description by way of example and with reference to the flow diagram accompanying the provisional specification of one method of carrying the present invention into effect.

The gas to be treated is a gas from which 80% of the hydrogen sulphide has already been removed by a primary liquid purification process using ammoniacal wash liquor but causing insignificant change in the ammonia content of the gas.

This gas contains:—

Hydrogen sulphide	-	-	80 grains H ₂ S per 100 cu.ft.
Hydrogen cyanide	-	-	40 grains HCN per 100 cu.ft.
Ammonia	-	-	220 grains NH ₃ per 100 cu.ft.

The plant for the secondary purification is represented by the accompanying flow diagram which shows that the gas is passed in succession through four sets of washers:—

The washers 1 for final zinc precipitation are provided for working up excess zinc liquor prior to ammonium sulphate recovery. They are a means of bringing this liquor into contact with a gas containing hydrogen sulphide to convert to insoluble zinc sulphide all the other zinc compounds present, the concentrations of ammonia and hydrogen cyanide present being such that the conversion to insoluble sulphide can be substantially complete, only about 5×10^{-4} grams atoms of zinc remaining in solution with about 2 gram molecules of ammonium sulphate in each litre (2M solution contains 264 gms. per litre or 23.3% of (NH₄)₂SO₄ by weight).

These washers are of the multistage type and the liquor is moved through them in a single pass countercurrent to the gas.

Only a small proportion of the total precipitation of zinc is effected in these washers which accordingly make small reductions in the concentrations of hydrogen sulphide and ammonia in the gas and a small increase in its hydrogen cyanide content.

The main washers 2 for secondary purification are similarly of the multi-stage type with countercurrent flow but with recirculation of liquor from the first to the last of the stages in contact with the gas. In these washers hydrogen sulphide is removed from the gas substantially completely and to below the statutory limit. The residual concentrations of ammonia and hydrogen cyanide in the treated gas are in the ranges 10 to 20 and 1

to 2 grains per 100 cu.ft. respectively.

The liquors in contact with the gas in all stages contain excess of soluble zinc, mainly in the form of amines, and sufficient ammonium sulphate to prevent the precipitation of zinc as hydroxide.

The liquor first brought in contact with the gas, that is with the outgoing gas in the last stage of the multi-stage concurrent system, is a mixture made in the mixing tank 6 and stored in the return tank 7. The pH of the mixture is controlled by variation of the rate of addition of 78% sulphuric acid to the regenerator 10, the control pH of about 8 being selected as high enough to ensure a reasonable reserve of alkalinity and just low enough to ensure that the ammonia vapour pressure of the liquor does not exceed 20 grains per 100 cu.ft.

The liquor last leaving contact with the gas at the first or gas-inlet stage is by compression richer in precipitated zinc sulphide and cyanide and in dissolved ammonium sulphate and unfixed ammonia, the pH is higher and the concentration of dissolved zinc is lower. This liquor passes to the slurry separator 5.

The washers 3 for final removal of ammonia and hydrogen cyanide also are of the multi-stage countercurrent-flow type with recirculation of liquor from the first gas-contacting stage to the last, in this case by way of the tank 8. Their normal function is the substantially complete removal of the residual 10 to 20 grains of ammonia per 100 cu.ft. and the residual 1 to 2 grains of hydrogen cyanide in the gas. Their reserve function is the removal of residual hydrogen sulphide slipping past the earlier washers during possible periods of partial failure or of overloading. The liquor in all stages is relatively dilute, almost neutral in pH, and contains an appreciable concentration of divalent zinc ions. The changes in concentration and pH from stage to stage are kept small by providing sufficient recirculation. At the liquor-entry or gas-outlet stage liquor is provided that is very slightly acid, sufficiently so to ensure negligible ammonia vapour pressure but not acid enough to corrode steel or iron.

The condenser 4 receives gas free from hydrogen sulphide, ammonia and hydrogen cyanide, but warm and saturated with water vapour because no special means have been provided in the earlier gas washing plant to remove the heat generated by the purification and other chemical reactions in the system and part of the heat added to the system for the evaporative crystallization of ammonium sulphate. The condenser cools the gas and condenses the excess water vapour, the purified gas leaving the system being cool but saturated with water vapour. The aqueous condensate removed from the gas is relatively clean and substantially neutral.

Referring to the flow of zinc liquors and slurries, the slurry separator 5 comprises a receiving tank for the liquor from the main washers 2, a system of cyclones to separate the liquor into a concentrated slurry of zinc sulphide and cyanide and a decant liquor containing little precipitate, and a small tank for decanted liquor. The concentrated slurry is passed direct to the regenerator 10 for treatment with sulphuric acid. The decanted liquor is divided, very much the greater part is returned for re-use in the main washers 2 by way of the tanks 6 and 7, and the small part is treated in the washers 1 for complete precipitation of the zinc as sulphide.

The mixing tank 6 receives all the liquors, not otherwise required or disposable, that can be mixed to form the liquor for re-use in the main washers 2.

These are:—

Decanted recycle liquor from the slurry separator 5.

Acidic zinc sulphate solution from the regenerator 10.

Condensate from the indirect-cooled condenser 14 for distillate leaving the stripping still.

Condensate from the indirect cooler 15 for the hydrogen sulphide gases.

Excess liquor from the tank 8 of the washers 3 for final ammonia removal.

The return tank 7 receives mixed liquor from the mixing tank 6 for re-use in the main washers 2.

The tank 8 for neutral zinc liquor serves the washers 3 for final removal of ammonia and hydrogen cyanide. It is divided into three sections. The receiving section takes the faintly alkaline liquor from the washers part of which is passed to the mixing tank 6, the remainder entering the second section. To this mixing section are added the acidic make-up of zinc sulphate solution and the diluent make-up of aqueous condensate from the condenser 4. The return section takes the mixed liquor for re-use in the washers.

The filter 9 is provided to separate zinc sulphide precipitate formed in the final zinc precipitation in the washers 1, from the zinc-free ammonium sulphate solution; it is a continuous filter, the precipitate being delivered unwashed as a slurry to the regenerator 10.

The regenerator 10 receives zinc sulphide slurry from the filter, zinc sulphide-cyanide slurry from the slurry separator and 78% sulphuric acid imported from outside the secondary purification system. It delivers zinc sulphate solution containing excess sulphuric acid, and hydrogen sulphide gas containing much hydrogen cyanide and some carbon dioxide.

To ensure that little hydrogen cyanide or hydrogen sulphide remains dissolved in the acidic zinc sulphate solution leaving the regenerator 10 steam is blown through the

zinc sulphate solution to heat it and to strip out dissolved gases.

Referring to the ammonium sulphate plant, the stripping still 11 receives clear ammonium sulphate solution from the filter together with mother liquor and washings from the centrifuge 13 and brings them into countercurrent contact with low pressure steam evaporated from the crystallizer 12. The ammonia, carbon dioxide, hydrogen sulphide and hydrogen cyanide dissolved in the ammonium sulphate solution are thereby carried away in the outgoing steam, removal of these components being desirable to prevent excessive corrosion in the crystallizer to which the stripped liquor passes. The outgoing steam passes to the stripping-steam condenser 14.

Measurement of the density of the stripped ammonium sulphate solution indicates the general level of sulphate concentrations in the system, which are adjusted by making small changes in the rate of withdrawal of liquor through the washers 1 to the filter 9 and correspondingly in the rate of return of aqueous condensate from the condenser 14 to the tank 6.

The evaporative crystallizer 12 receives ammonium sulphate solution free from impurities volatile in steam and effects continuous crystallization by evaporation of excess water. Heating is by indirect steam. Most of the steam driven off is passed directly through the stripping still 11; a small part passes into the regenerator 10. Ammonium sulphate crystals settle out and are removed periodically to the batch centrifuge 13.

The centrifuge 13 receives batches of ammonium sulphate crystals as a slurry and removes the mother liquor. The crystals are washed with part of the aqueous condensate from the hot well of the washer-cooler 4. Mother liquor and washings are return to the crystallizer 12 indirectly as part of the feed to the stripping still 11. The washed and whizzed crystals are removed for drying and bagging elsewhere.

The condenser 14 for stripping steam is an indirect cooled with upward flow of steam, downward reflux of condensate and downward flow of cooling water. The condensate passes to the mixing tank 6; permanent gases pass overhead and return to the unpurified coal gas stream.

The indirect cooler 15 for hydrogen sulphide gases, also with upward flow of the feed and downward flow of condensate and cooling water, cools the hydrogen sulphide gases passing out overhead and removes most of its water vapour content. It effects a considerable degree of rectification so that the reflux condensate which passes hot to the mixing tank 6 does not take with it any appreciable recycle quantity of either hydrogen sulphide or hydrogen cyanide.

WHAT WE CLAIM IS:—

1. A process for the simultaneous removal of hydrogen sulphide and hydrogen cyanide from fuel gas which process comprises washing the gas with a weakly ammoniacal zinc sulphate solution containing sufficient ammonium sulphate to prevent the precipitation of zinc hydroxide, separating the precipitated zinc sulphide and insoluble cyanogen compounds of zinc from the resultant solution, processing the said solution for the recovery of crystalline ammonium sulphate substantially free from zinc compounds, and reconverting said precipitate to zinc sulphate for re-use in the process.

2. A process as claimed in Claim 1 wherein the fuel gas is coal gas or coke-oven gas.

3. A process as claimed in Claim 2 wherein the hydrogen sulphide concentration is reduced below the statutory limit for town gas.

4. A process as claimed in any one of the preceding claims wherein the fuel gas contains an amount of ammonia at least equivalent to the hydrogen sulphide and hydrogen cyanide removed.

5. A process as claimed in any one of Claims 1 to 3 wherein additional ammonia is added to the fuel gas.

6. A process as claimed in any one of Claims 1 to 3 wherein additional ammonia is added to the zinc sulphate solution as concentrated ammoniacal liquor.

7. A process as claimed in any one of Claims 1 to 4 wherein the fuel gas to be treated is initially washed with an ammoniacal solution to remove the major proportion of the hydrogen sulphide present said washing being carried out in such a manner that the ammonia concentration in the partially purified gas is at least equivalent to the hydrogen sulphide and hydrogen cyanide to be removed.

8. A process as claimed in any one of the preceding claims wherein during the washing with the ammoniacal zinc sulphate solution the greater part of the wash liquor is continuously recirculated, the greater part of the precipitated zinc compounds being removed after each wash.

9. A process as claimed in Claim 8 wherein the wash liquor to be recirculated after removal of substantially all of the precipitated zinc compounds is mixed with regenerated zinc sulphate solution and ammoniacal liquor in order that the composition of the wash liquor may not vary greatly.

10. A process as claimed in any one of the preceding claims wherein the ammonium sulphate is recovered from the resultant solution by treating the solution in order to precipitate all the zinc in solution as zinc sulphide, filtering to separate the zinc sulphide and thereafter stripping the filtrate with steam to remove any volatile corrosive impurities and converting the ammonium sulphate solution to a crystalline salt in an evaporative crystallizer.

11. A process as claimed in Claim 10

wherein the resultant solution is treated with hydrogen sulphide, ammonium sulphide or ammonium hydrosulphide.

12. A process as claimed in Claim 10 wherein the resultant solution is treated with concentrated ammoniacal liquor rich in dissolved hydrogen sulphide.

13. A process as claimed in Claim 10 wherein the resultant solution is treated with unpurified coal gas or coke-oven gas or a similar gas which has been partially purified from hydrogen sulphide by washing with aqueous ammonia.

14. A process as claimed in any one of the preceding claims wherein zinc sulphate is obtained from the precipitate separated from the wash liquor by washing the precipitate to reduce its content of ammonium sulphate and thereafter roasting the precipitate in a fluidised bed with sulphur or hydrogen sulphide equivalent to the cyanogen compounds of zinc present and to the required excess of sulphur to

ensure substantially complete conversion of all the zinc to zinc sulphate.

15. A process as claimed in any one of Claims 1 to 13 wherein zinc sulphate is obtained from the precipitate separated from the wash liquor by dissolving the precipitate in sulphuric acid, at least two equivalents of acid being used for each equivalent of zinc.

16. A process as claimed in any one of the preceding claims wherein the gas after removal of hydrogen sulphide and hydrogen cyanide therefrom is washed with water, sulphuric acid, or regenerated zinc sulphate solution in order to remove any residual ammonia in the gas.

17. A process for the simultaneous removal of hydrogen sulphide and hydrogen cyanide from the fuel gas substantially as described in the specific example with reference to the drawing filed with the provisional specification.

BOULT, WADE & TENNANT,

111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.

PROVISIONAL SPECIFICATION

Improvements in or relating to the Purification of 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 improvements in or relating to the purification of gases and is particularly concerned with the purification of fuel gases, e.g. coal gas or coke-oven gas, from which both hydrogen sulphide and hydrogen cyanide must be removed. The invention is particularly applicable to gases which also contain ammonia that must be removed.

It is an object of the present invention to reduce the hydrogen sulphide concentration in a fuel gas to a very low level, for example below the statutory limit for town gas approximately 0.7 parts per million by volume.

A further object of the present invention is to reduce the hydrogen cyanide concentration in a fuel gas to a low level, for example, below 5 grains per 100 cu.ft.

There have been a number of known processes for the removal of hydrogen sulphide from gases by the use of zinc sulphate solution. These processes were all characterised by a purification stage which may be represented as:—

$2\text{NH}_3 + \text{ZnSO}_4 + \text{H}_2\text{S} = \text{ZnS} + (\text{NH}_4)_2\text{SO}_4$,
by the separation of the zinc sulphide precipitate, and by the reversion of this sulphide to zinc sulphate for re-use in the process. Emphasis was laid upon the complete removal of ammonia from the gas and its recovery as pure ammonium sulphate. The regenerated zinc sulphate solution in most of these processes tended to be acid.

There is no disclosure in the known art of the use of zinc sulphate solution for the sub-

stantially complete removal of hydrogen sulphide from a gas with full regeneration and re-use of the zinc sulphate reagent, the emphasis being on conditions which are unsuitable for complete purification. One condition for complete purification is that the zinc sulphate solution should be alkaline. However, the presence of alkali is objectionable for the following two reasons: (a) the zinc ions tend to be removed from solutions as precipitated zinc hydroxide or carbonate and are thereby made ineffective for the removal of hydrogen sulphide and (b) the zinc ions tend to react with any hydrogen cyanide present to form soluble compound ions which are not effective for complete hydrogen sulphide removal and which may make it very difficult to operate the process to obtain an ammonium sulphate product that is free from zinc.

A well-known method for the analysis of gases for hydrogen sulphide and hydrogen cyanide concentration employs strongly ammoniacal zinc sulphate solution in such manner that these two components are completely removed from the gas and remain with the reagent respectively as precipitated zinc sulphide and soluble ammonium zincicyanide.

This and further known properties of the cyanogen compounds of zinc would lead those skilled in the art to predict that the known processes could not readily be applied to a gas containing hydrogen cyanide to produce ammonium sulphate free from soluble zinc compounds.

To secure a substantial removal of hydrogen cyanide by a continuous process with full regeneration and re-use of the zinc sulphate reagent it is necessary to establish conditions in which an insoluble cyanogen compound is

formed; this can then be separated and subjected to a chemical treatment to regenerate the reagent quantitatively.

5 The equilibria in ammoniacal solutions of zinc sulphate used for the absorption of hydrogen cyanide are represented by equilibrium constants published in the literature. No calculation from these known constants predicts the formation of an insoluble cyanogen
10 compound of zinc under any conditions likely to be useful in a continuous process for the removal of hydrogen cyanide from gas with full regeneration and re-use of the zinc sulphate reagent.

15 In contrast to this prediction from the known constants we have found by experiment that if weakly ammoniacal zinc sulphate is used to remove hydrogen sulphide from gas containing also hydrogen cyanide, the precipitation of cyanogen compounds of zinc is very considerable indeed. This phenomenon is associated with the simultaneous precipitation of zinc sulphide and would not otherwise occur. The sulphide precipitate is known to
20 occlude much foreign matter, but the co-precipitation of cyanogen compounds is quite exceptional.

If small quantities of ammonia are added to neutral zinc sulphate solution, zinc
30 hydroxide is precipitated. If more ammonia is added, the zinc hydroxide redissolves, most of the zinc in solution being combined with ammonia as ions of the ammine type. In a solution containing about 3% ZnSO_4 by weight the precipitation of zinc hydroxide is prevented by the addition of enough ammonia to raise the pH above 10. If a substantial concentration of ammonium sulphate is present the pH may be much lower without the
40 precipitation of zinc hydroxide. Such liquors, if very rich in ammonium sulphate, may be free from insoluble zinc hydroxide and have a low ammonia vapour pressure, for example, less than 5 grains NH_3 per 100 cu.ft. at 20°
45 C.

The weakly ammoniacal zinc sulphate solutions employed in the process of the present invention are such that they contain sufficient ammonium sulphate to prevent the precipitation of zinc hydroxide. The free ammonia content is however sufficiently low to permit them to be employed in the process so that the resulting purified gas contains not more than 50 grains NH_3 per 100 cu.ft. and preferably not more than 20 grains.
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The concentration of salts present is preferably high but not so high that the separation of crystals of zinc ammonium sulphate becomes possible.

60 According to the present invention there is provided a process for the simultaneous removal of hydrogen sulphide and hydrogen cyanide from fuel gas which process comprises washing the gas with a weakly ammoniacal
65 zinc sulphate solution containing sufficient

ammonium sulphate to prevent the precipitation of zinc hydroxide, separating the precipitated zinc sulphide and insoluble cyanogen compounds of zinc from the resultant solution, processing the said solution for the recovery
70 of crystalline ammonium sulphate substantially free from zinc compounds, and reconvertng said precipitate to zinc sulphate for re-use in the process.

The process is particularly suitable for the treatment of coal gas and coke-oven gas and is preferably applied to such gases so that the greater part of their ammonia content is removed simultaneously with the hydrogen sulphide and hydrogen cyanide.
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The process of the present invention consumes ammonia equivalent to the hydrogen sulphide and hydrogen cyanide removed; a further quantity of ammonia may be needed to bring the regenerated zinc sulphate solution to the necessary ammoniacal condition. Where insufficient ammonia is present in the gas to be treated, for example, additional quantities may be added to the system, for example, directly to the zinc sulphate solution as concentrated ammoniacal liquor.
85 90

In one preferred application of the present invention coal gas or coke-oven gas to be purified is washed in a primary purification process with an ammoniacal solution for the removal of the major proportion, e.g. 80% of the hydrogen sulphide present in such manner that little change is effected in the ammonia concentration in the gas which is accordingly more than the equivalent of the hydrogen sulphide and hydrogen cyanide in the gas. The present process is then applied for secondary purification of the gas to remove all the remaining hydrogen sulphide and most of the hydrogen cyanide and ammonia.
100 105

In one preferred method of washing the gas the greater part of the wash liquor is continuously recirculated so that the change in the composition of the wash liquor on one passage through the washer is relatively small. With this system by removing the greater part of the precipitate, present after one passage of the liquor through the washer, before returning the liquor to the washer it is possible to combine a high concentration of ammonium sulphate in the wash liquor with a low content of precipitate in the washer; the concentration of ammonium sulphate also becomes large in relation to the concentration of unfixed ammonia present with it in the liquor
110 115 120 125 130

Conditions resulting from the recirculation method are therefore favourable for maintaining the desired high proportion of ammonium sulphate and for the processing of the excess volume of liquid for the production of crystalline ammonium sulphate. The recirculated wash liquor after substantial reduction of its content of precipitate but before returning to the washer may be mixed with regenerated zinc sulphate solution and ammoniacal liquids

so that the liquid entering the washer does not vary greatly in composition.

The ammonium sulphate may be recovered from the wash liquor after the separation of the precipitated zinc sulphide and insoluble cyanogen compounds of zinc by treating the wash liquor to convert all the zinc remaining in solution to insoluble zinc sulphide, filtering to separate the zinc sulphide and thereafter stripping the filtrate with steam to remove volatile impurities and converting the ammonium sulphate solution to the crystalline salt in an evaporative crystalliser.

To effect this final precipitation of soluble zinc the wash liquor may be treated with hydrogen sulphide, ammonium sulphide or ammonium hydrosulphide. The sulphiding agent may contain hydrogen cyanide, but this must be in low absolute concentration; thus the hydrogen sulphide gases produced in the process when using the acid method for regeneration of the zinc sulphate reagent is unsuitable because of the high partial pressure of hydrogen cyanide present. Suitable reagents include concentrated ammoniacal liquor which is rich in dissolved hydrogen sulphide, unpurified coal gas or coke-oven gas, or similar gases from which the major proportion of hydrogen sulphide, e.g. 80%, has been removed by washing with aqueous ammonia.

It is preferable that the wash liquor sulphided in this manner should be initially free from precipitate containing cyanogen compounds of zinc, but if such precipitate is present the sulphiding treatment is likely to convert the insoluble cyanogen compounds to zinc sulphide.

It is important that the quantity of zinc precipitated as sulphide in processing the wash liquor for ammonium sulphate recovery should be small in proportion to that separated from the wash liquor used in the main washing stage. The removal of the precipitate from the main washing stage is the only substantial purge of cyanogen compounds from the washing system. Thus the continued removal of hydrogen cyanide from the gas is dependent upon the separation of this precipitate.

Hydrogen sulphide	-	-
Hydrogen cyanide	-	-
Ammonia	-	-

The plant for the secondary purification is represented by the accompanying flow diagram which shows that the gas is passed in succession through four sets of washers:—

The washers 1 for final zinc precipitation are provided for working up excess zinc liquor prior to ammonium sulphate recovery. They are a means of bringing this liquor into contact with a gas containing hydrogen sulphide to convert to insoluble zinc sulphide all the other zinc compounds present, the concentrations of ammonia and hydrogen cyanide present being such that the conversion to insoluble sulphide

For the regeneration of zinc sulphate from the wash liquor two methods are available. The precipitate may be washed to reduce its content of ammonium sulphate and thereafter fed to a roaster, preferably as a slurry, and roasted in a fluidised bed with sulphur or hydrogen sulphide equivalent to the cyanogen compounds of zinc present and to the excess of sulphur required to ensure substantially complete conversion of all the zinc to zinc sulphate. Alternatively, the zinc sulphate may be obtained from the precipitate separated from the wash liquor by dissolving the precipitate in sulphuric acid, at least two equivalents of acid being necessary for each equivalent of zinc.

The gas after removal of hydrogen sulphide and hydrogen cyanide therefrom may be subjected to a final wash employing water, sulphuric acid or regenerated zinc sulphate solution in order to remove any residual ammonia in the gas. The used washing medium may be mixed with liquid recirculated in the main washing stage.

Heat is generated by the chemical reactions involved in the process; means of removing the heat may be desirable. A preferred method is to allow this heat to be carried forward in the gas as sensible heat and as the latent heat of water of saturation; the cooling may then be effected in a condenser and the aqueous condensate returned to the process to the extent and to the places which will give the best control of the water balance of the process and of the concentration levels of the aqueous solutions employed.

Following is a description by way of example and with reference to the accompanying flow diagram of one method of carrying the present invention into effect.

The gas to be treated is a gas from which 80% of the hydrogen sulphide has already been removed by a primary liquid purification process using ammoniacal wash liquor but causing insignificant change in the ammonia content of the gas.

This gas contains:—

80 grains H_2S per 100 cu.ft.
40 grains HCN per 100 cu.ft.
220 grains NH_3 per 100 cu.ft.

can be substantially complete, only about 5×10^{-4} gram atoms of zinc remaining in solution with about 2 gram molecules of ammonium sulphate in each litre (2M solution contains 264 gms. per litre or 23.3% of $(NH_4)_2SO_4$ by weight).

These washers are of the multi-stage type and the liquor is moved through them in a single pass countercurrent to the gas.

Only a small proportion of the total precipitation of zinc is effected in these washers which accordingly make small reductions in the concentrations of hydrogen sulphide and

ammonia in the gas and a small increase in its hydrogen cyanide content.

The main washers 2 for secondary purification are similarly of the multi-stage type with countercurrent flow but with recirculation of liquor from the first to the last of the stages in contact with the gas. In these washers hydrogen sulphide is removed from the gas substantially completely and to below the statutory limit. The residual concentrations of ammonia and hydrogen cyanide in the treated gas are in the ranges 10 to 20 and 1 to 2 grains per 100 cu.ft. respectively.

The liquors in contact with the gas in all stages contain excess of soluble zinc, mainly in the form of amines, and sufficient ammonium sulphate to prevent the precipitation of zinc as hydroxide.

The liquor first brought in contact with the gas, that is with the outgoing gas in the last stage of the multi-stage concurrent system, is a mixture made in the mixing tank 6 and stored in the return tank 7. The pH of the mixture is controlled by variation of the rate of addition of 78% sulphuric acid to the regenerator 10, the control pH of about 8 being selected as high enough to ensure a reasonable reserve of alkalinity and just low enough to ensure that the ammonia vapour pressure of the liquid does not exceed 20 grains per 100 cu.ft.

The liquor last leaving contact with the gas at the first or gas-inlet stage is by comparison richer in precipitated zinc sulphide and cyanide and in dissolved ammonium sulphate and unfixed ammonia, the pH is higher and the concentration of dissolved zinc is lower. This liquor passes to the slurry separator 5.

The washers 3 for final removal of ammonia and hydrogen cyanide also are of the multi-stage countercurrent-flow type with recirculation of liquor from the first gas-contacting stage to the last, in this case by way of the tank 8. Their normal function is the substantially complete removal of the residual 10 to 20 grains of ammonia per 100 cu.ft. and the residual 1 to 2 grains of hydrogen cyanide in the gas. Their reserve function is the removal of residual hydrogen sulphide slipping past the earlier washers during possible periods of partial failure or of overloading. The liquor in all stages is relatively dilute, almost neutral in pH, and contains an appreciable concentration of divalent zinc ions. The changes in concentration and pH from stage to stage are kept small by providing sufficient recirculation. At the liquor-entry or gas-outlet stage liquor is provided that is very slightly acid, sufficiently so to ensure negligible ammonia vapour pressure but not acid enough to corrode steel or iron.

The condenser 4 receives gas free from hydrogen sulphide, ammonia and hydrogen cyanide, but warm and saturated with water vapour because no special means have been

provided in the earlier gas washing plant to remove the heat generated by the purification and other chemical reactions in the system and part of the heat added to the system for the evaporative crystallization of ammonium sulphate. The condenser cools the gas and condenses the excess water vapour, the purified gas leaving the system being cool but saturated with water vapour. The aqueous condensate removed from the gas is relatively clean and substantially neutral.

Referring to the flow of the zinc liquors and slurries, the slurry separator 5 comprises a receiving tank for the liquor from the main washers 2, a system of cyclones to separate the liquor into a concentrated slurry of zinc sulphide and cyanide and a decant liquor containing little precipitate, and a small tank for decanted liquor. The concentrated slurry is passed direct to the regenerator 10 for treatment with sulphuric acid. The decanted liquor is divided, very much the greater part is returned for re-use in the main washers 2 by way of the tanks 6 and 7, and the small part is treated in the washers 1 for complete precipitation of the zinc as sulphide.

The mixing tank 6 receives all the liquors, not otherwise required or disposable, that can be mixed to form the liquor for re-use in the main washers 2. These are:—

Decanted recycle liquor from the slurry separator 5.

Acidic zinc sulphate solution from the regenerator 10.

Condensate from the indirect-cooled condenser 14 for distillate leaving the stripping still.

Condensate from the indirect cooler 15 for the hydrogen sulphide gases.

Excess liquor from the tank 8 of the washers 3 for final ammonia removal.

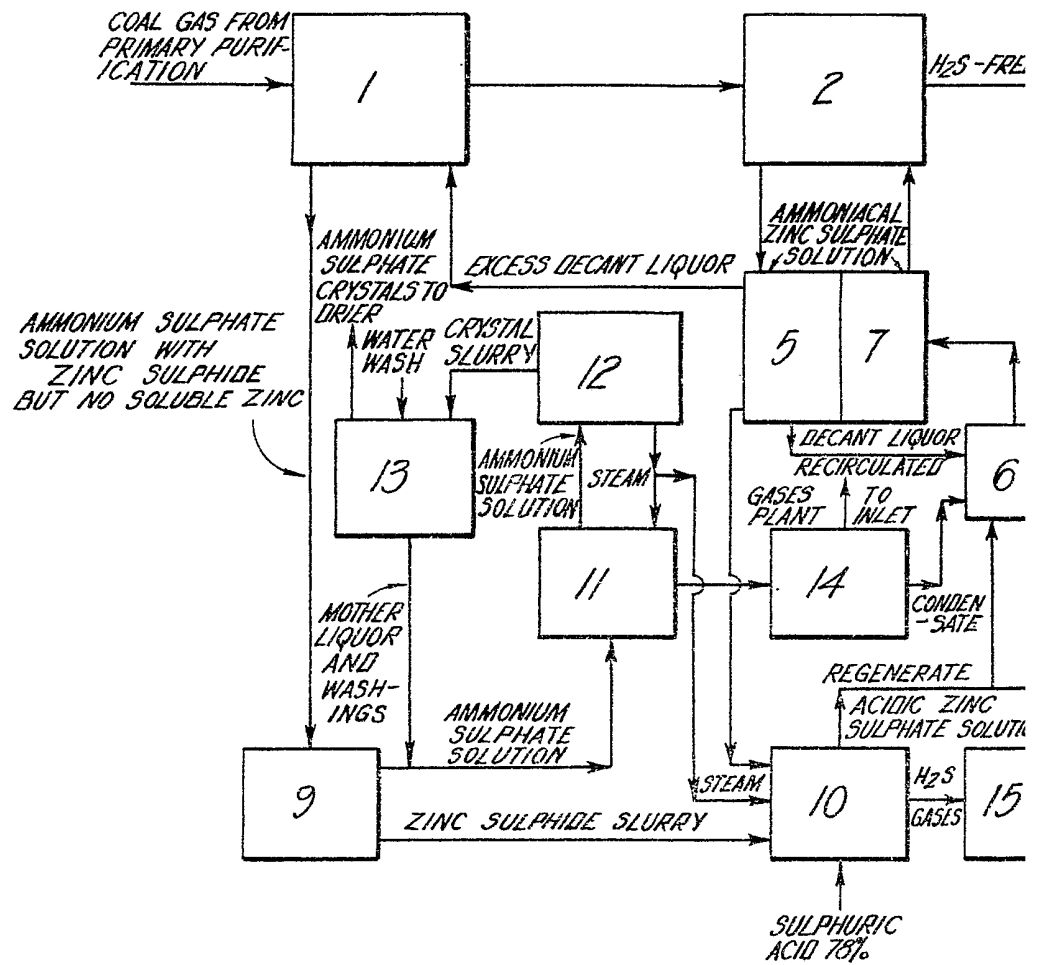
The return tank 7 receives mixed liquor from the mixing tank 6 for re-use in the main washers 2.

The tank 8 for neutral zinc liquor serves the washers 3 for final removal of ammonia and hydrogen cyanide. It is divided into three sections. The receiving section takes the faintly alkaline liquor from the washers part of which is passed to the mixing tank 6, the remainder entering the second section. To this mixing section are added the acidic make-up of zinc sulphate solution and the diluent make-up of aqueous condensate from the condenser 4. The return section takes the mixed liquor for re-use in the washers.

The filter 9 is provided to separate zinc sulphide precipitate formed in the final zinc precipitation in the washers 1, from the zinc-free ammonium sulphate solution; it is a continuous filter, the precipitate being delivered unwashed as a slurry to the regenerator 10.

The regenerator 10 receives zinc sulphide slurry from the filter, zinc sulphide-cyanide slurry from the slurry separator and 78% sul-

- phuric acid imported from outside the secondary purification system. It delivers zinc sulphate solution containing excess sulphuric acid, and hydrogen sulphide gas containing much hydrogen cyanide and some carbon dioxide. 5
- To ensure that little hydrogen cyanide or hydrogen sulphide remains dissolved in the acidic zinc sulphate solution leaving the regenerator 10 steam is blown through the zinc sulphate solution to heat it and to strip out dissolved gases. 10
- Referring to the ammonium sulphate plant, the stripping still 11 receives clear ammonium sulphate solution from the filter together with mother liquor and washings from the centrifuge 13 and brings them into countercurrent contact with low pressure steam evaporated from the crystallizer 12. The ammonia, carbon dioxide, hydrogen sulphide and hydrogen cyanide dissolved in the ammonium sulphate solution are thereby carried away in the outgoing steam, removal of these components being desirable to prevent excessive corrosion in the crystallizer to which the stripped liquor passes. The outgoing steam passes to the stripping-steam condenser 14. 15
- Measurement of the density of the stripped ammonium sulphate solution indicates the general level of sulphate concentrations in the system, which are adjusted by making small changes in the rate of withdrawal of liquor through the washers 1 to the filter 9 and correspondingly in the rate of return of aqueous condensate from the condenser 14 to the tank 6. 20
- The evaporative crystallizer 12 receives ammonium sulphate solution free from impurities volatile in steam and effects continuous crystallization by evaporation of excess water. Heating is by indirect steam. Most of the steam driven off is passed directly through the stripping still 11; a small part passes into the regenerator 10. Ammonium sulphate crystals settle out and are removed periodically to the batch centrifuge 13. 40
- The centrifuge 13 receives batches of ammonium sulphate crystals as a slurry and removes the mother liquor. The crystals are washed with part of the aqueous condensate from the hot well of the washer-cooler 4. Mother liquid and washings are returned to the crystallizer 12 indirectly as part of the feed to the stripping still 11. The washed and whizzed crystals are removed for drying and bagging elsewhere. 45
- The condenser 14 for stripping steam is an indirect cooler with upward flow of steam, downward reflux of condensate and downward flow of cooling water. The condensate passes to the mixing tank 6; permanent gases pass overhead and return to the unpurified coal gas stream. 50
- The indirect cooler 15 for hydrogen sulphide gases, also with upward flow of the feed and downward flow of condensate and cooling water, cools the hydrogen sulphide gases passing out overhead and removes most of its water vapour content. It effects a considerable degree of rectification so that the reflux condensate which passes hot to the mixing tank 6 does not take with it any appreciable recycle quantity of either hydrogen sulphide or hydrogen cyanide. 55
- BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents. 60



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