PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to Gas Purification

We, SIMON-CARVES LIMITED, of Cheadle Heath, Stockport, County of Chester, a British Company 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 relates to improvements in or relating to gas purification.

Certain gases from industrial processes contain hydrogen cyanide and efficient and economic removal of this toxic constituent has at times presented a problem.

It is an object of the invention to provide an improved method of purifying a gas containing hydrogen cyanide.

Examples of gases which may contain hydrogen cyanide include coke oven gas, blast furnace gas and gas from continuous vertical retorts.

The invention provides a method of purifying a gas containing hydrogen cyanide, comprising the steps of removing hydrogen cyanide by reacting it with ammonia, hydrogen sulphide, sulphur and water, and reacting the reaction product with sulphuric acid under pressure.

The invention also provides a method of purifying a gas containing hydrogen cyanide and hydrogen sulphide, comprising the steps of removing hydrogen cyanide from the gas by reaction with ammonia and hydrogen sulphide, sulphur and water, and recovering sulphur from the hydrogen sulphide left in the gas after removal of the hydrogen cyanide.

The invention also provides a method of purifying a gas containing hydrogen cyanide wherein hydrogen cyanide is removed by reacting it with ammonia, hydrogen sulphide, sulphur which has been precipitated in an aqueous medium, and water.

The invention also provides a method of purifying a gas containing hydrogen cyanide comprising the steps of removing hydrogen cyanide by reacting it with ammonium polysulphide, and reacting the reaction product with sulphuric acid under pressure.

The invention also provides a method of purifying a coke oven gas containing hydrogen cyanide, hydrogen sulphide and ammonia comprising the steps of removing hydrogen cyanide by scrubbing the gas with an aqueous suspension of sulphur, autoclaving the reaction product with sulphuric acid to produce ammonium sulphate, recovering sulphur from hydrogen sulphide remaining in gas from the autoclaving step to provide an aqueous suspension of sulphur, and recycling a portion of said aqueous suspension to said scrubbing step.

In reacting hydrogen cyanide with ammonia, hydrogen sulphide, sulphur and water, it appears that ammonium polysulphide is formed which reacts with the hydrogen cyanide, to form a reaction product comprising ammonium thiocyanate. In autoclaving the reaction product with sulphuric acid; ammonium sulphate, carbon dioxide and hydrogen sulphide are formed.

It is believed that the following chemical reactions take place: —

(1) $2NH_4OH + H_2S + (x - 1)S \rightarrow (NH_4)_2S_x + 2H_2O$

(2) $(NH_4)_2S_x + 2HCN \rightarrow 2NH_4CNS + H_2S + (x - 3)S$

(3) $NH_4CNS + 2H_2O + H_2SO_4 \rightarrow (NH_4)_2 SO_4 + CO_2 + H_2S$

It appears that sulphur which has been precipitated in an aqueous medium is in an optimum state of wettability and subdivision for reaction (1) above and shows excellent activity for this reaction.

Preferably the hydrogen cyanide is reacted with the ammonia, hydrogen sulphide, sulphur and water at approximately ambient temperature and under approximately atmospheric pressure; if the gas is too hot there is insufficient retention of ammonia in aqueous solution. Where the gas contains ammonia this ammonia may be used for the reaction.

Preferably the sulphur is provided in an aqueous paste comprising between 1% and 7% by weight of sulphur, at least 80% of the sulphur being of particle size under 5 microns, between 100 and 5,000 times the stoichiometric quantity of sulphur according to reactions (1) and (2) is used, and the stoichiometric quantity of sulphuric acid according to reaction (3) or a slight excess is used.

Preferably the autoclaving is carried out at a temperature between 250°F and 450°F, under a pressure between 40 p.s.i.g. and 150 p.s.i.g.

There now follows a description of the process embodying the invention. This description is given by way of example of the invention only and not by way of limitation thereof, and is to be read with reference to the drawing, accompanying the provisional specification, which shows a flow diagram of the process.

The apparatus forms part of a coke oven plant and is adapted for use in purifying a coke oven gas containing hydrogen sulphide, ammonia and hydrogen cyanide, and comprises a scrubber 12 packed randomly with Raschig rings; the gas enters the scrubber 12 by a line 14 to be scrubbed for the removal of hydrogen cyanide by liquor comprising an aqueous suspension of sulphur which has been precipitated in "Stretford" sulphur recovery equipment 13; the liquor enters the scrubber 12 by a line 16. We believe that reactions (1) and (2) take place in the scrubber 12. The gas leaves the scrubber 12 by a line 18 and the liquor leaves by a line 20.

The line 20 leads to a still 21 where hydrogen sulphide and ammonia are stripped from the liquor. The hydrogen sulphide and ammonia are recycled to the line 14 through a line 23. The liquor leaves the still 21 by a line 25.

The line 25 leads to a settling tank 22 where sulphur paste is separated from the liquor. The sulphur paste is recycled from the tank 22 to the scrubber 12 through the line 16; make-up water is added through a line 17 leading into the line 16. The clear liquor leaves the tank 22 through a line 26.

The line 26 leads to a batch autoclave 24 where the liquor is autoclaved with highly concentrated sulphuric acid which enters the autoclave 24 through a line 28. We believe that reaction (3) takes place in the autoclave 24. The liquor leaves the autoclave 24 through a line 30 and gas leaves the autoclave 24 by a line 32 which leads to the line 18.

The line 30 leads to equipment 34 for the crystallisation of ammonium sulphate from the liquor.

The line 18 leads to equipment 35 of known type for the removal of ammonia from the gas and the gas leaves the equipment 35 by a line 37.

The line 37 leads to the equipment 13 where elemental sulphur is recovered from hydrogen sulphide. The equipment 13 comprises a washer 36 where the gas from the line 37 is scrubbed for the removal of hydrogen sulphide by an aqueous alkaline solution comprising sodium salts of antraquinone disulphonic acids and sodium vanadate. The solution enters the scrubber 36 through a line 38 and leaves through a line 40. The gas leaves through a line 43.

The line 40 leads to an aeration tank 42 in which the solution is aerated. An aerator 44 is mounted in the tank 42 and this aerator 44 is substantially as described in U.K. patent specification No. 919,467. An aqueous paste of precipitated sulphur is separated from the solution and leaves the tank 42 through a line 46 and the solution, substantially free from sulphur, is recycled from the tank 42 to the scrubber 36 through the line 38.

A line 48 leads from the line 46 to the line 16 and a portion of the aqueous sulphur paste is recycled along the line 48 to provide make-up sulphur for the scrubber 12.

It will be realised that various modifications of the apparatus are possible; for example, in some circumstances it may be possible to omit the still 21; also, for example, the settling tank 22 may be replaced by a filter.

EXAMPLE I

Coke oven gas:—

HCN	1583	p.p.m.
NH_3	4262	p.p.m.
H_2S	6300	p.p.m.

Aqueous suspension of sulphur S — 4% precipitated in equipment corresponding to the equipment 13.

Particle size distribution:—

Size (Microns)	% by weight undersize
5.0	93
4.0	88
3.0	80
2.5	75
2.0	66
1.75	60
1.5	53
1.25	44
1.0	36
0.75	25
0.5	14
0.25	4

The particle size distribution was determined in apparatus substantially as described in the complete specification of our U.K. patent specification No. 1,023,441.

1,590 cubic feet per hour of the coke oven gas were scrubbed with 8 gallons per minute of the sulphur suspension.

After scrubbing the gas composition included: —

HCN	143	p.p.m.
NH_3	2401	p.p.m.
H_2S	4910	p.p.m.

The liquor after scrubbing was treated in an autoclave with concentrated sulphuric acid at a temperature of 280°F and under a pressure of 45 p.s.i.g. Apparently stoichiometric conversion of ammonium thiocyanate to ammonium sulphate was obtained.

EXAMPLE II

Coke oven gas: —

HCN	1306	p.p.m.
NH_3	3722	p.p.m.
H_2S	6660	p.p.m.

Aqueous suspension of sulphur: —

As in Example I.

1,590 cubic feet per hour of the coke oven gas were scrubbed with 8 gallons per minute of the sulphur suspension.

After scrubbing, the gas composition included: —

HCN	122	p.p.m.
NH_3	1836	p.p.m.
H_2S	5609	p.p.m.

The liquor after scrubbing was treated in an autoclave with concentrated sulphuric acid at a temperature of 350°F and under a pressure of 125 p.s.i.g. Apparently about 94% conversion to ammonium sulphate was obtained.

EXAMPLE III

The procedure of Example II was substantially repeated, autoclaving being carried out at a temperature of 350°F and under a pressure of 140 p.s.i.g. Apparently about 97.5% conversion to ammonium sulphate was obtained.

WHAT WE CLAIM IS: —

1. A method of purifying a gas containing hydrogen cyanide, comprising the steps of removing hydrogen cyanide by reacting it with ammonia, hydrogen sulphide, sulphur and water, and reacting the reaction product with sulphuric acid under pressure.

2. A method according to claim 1 wherein between 100 and 5,000 times the stoichiometric quantity of sulphur according to reactions (1), (2) and (3) as hereinbefore described is used and the stoichiometric quantity of sulphuric acid according to reaction (3) or a slight excess is used.

3. A method according to claim 1 or claim 2 wherein the reaction with sulphuric acid is carried out at a temperature between 250°F and 450°F, under a pressure between 40 p.s.i.g. and 150 p.s.i.g.

4. A method of purifying a gas containing hydrogen cyanide and hydrogen sulphide, comprising the steps of removing hydrogen cyanide from the gas by reaction with ammonia, and hydrogen sulphide, sulphur and water and recovering sulphur from the hydrogen sulphide left in the gas after removal of the hydrogen cyanide.

5. A method of purifying a gas containing hydrogen cyanide, wherein hydrogen cyanide is removed by reacting it with ammonia, hydrogen sulphide, sulphur which has been precipitated in an aqueous medium and water.

6. A method according to any one of claims 4, 5 and 6 wherein between 100 and 5,000 times the stoichiometric quantity of sulphur according to reactions (1) and (2) as hereinbefore described is used.

7. A method according to any one of claims 1, 2, 3 and 5 wherein the sulphur is recovered from hydrogen sulphide originally present in the gas.

8. A method according to claim 4, or claim 7 wherein the sulphur is recovered from hydrogen sulphide by contacting the hydrogen sulphide with an aqueous alkaline solution comprising sodium salts of anthraquinone disulphonic acids and sodium vanadate, aerating the solution, and separating an aqueous sulphur paste from the solution which solution is then recycled for further contacting.

9. A method according to any one of claims 1 to 3, wherein the sulphur has been precipitated in an aqueous medium.

10. A method according to claim 5 or claim 9 wherein the sulphur is employed in the aqueous medium in which it is precipitated.

11. A method according to any one of the preceding claims wherein said sulphur and water are provided as an aqueous paste comprising between 1% and 7% by weight of sulphur, at least 80% of the sulphur being of particle size under 5 microns.

12. A method according to any one of the preceding claims wherein the reaction

between hydrogen cyanide, ammonia, hydrogen sulphide, sulphur and water is carried out at approximately ambient temperature and under approximately atmospheric pressure.

13. A method according to any one of the preceding claims wherein said ammonia is provided by the gas to be purified.

14. A method of purifying a gas containing hydrogen cyanide comprising the steps of removing hydrogen cyanide by reacting it with ammonium polysulphide, and reacting the reaction product with sulphuric acid under pressure.

15. A method according to claim 14 wherein the reaction with sulphuric acid is carried out at a temperature between 250°F and 450°F, under a pressure between 40 p.s.i.g. and 150 p.s.i.g.

16. A method according to claim 14 or claim 15 wherein the reaction between hydrogen cyanide and ammonium polysulphide is carried out at approximately ambient temperature and under approximately atmospheric pressure.

17. A method according to any one of the preceding claims wherein said gas is a coke oven gas.

18. A method of purifying a coke oven gas containing hydrogen cyanide, hydrogen sulphide and ammonia, comprising the steps of removing hydrogen cyanide by scrubbing the gas with an aqueous suspension of sulphur, autoclaving the reaction product with sulphuric acid to produce ammonium sulphate, recovering sulphur from hydrogen sulphide remaining in gas from the autoclaving step to provide an aqueous suspension of sulphur, and recycling a portion of said aqueous suspension to said scrubbing step.

19. Gas when purified by a method according to any one of the preceding claims.

20. A method of purifying gas substantially as hereinbefore described with reference to any one of Examples I, II and III.

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1101379 PROVISIONAL SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*