

# PATENT SPECIFICATION

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(72) Inventor DAVID MICHAEL SINGLETON

## (54) A PROCESS FOR THE CATALYTIC INCINERATION OF HYDROGEN SULPHIDE-CONTAINING WASTE GASES AND A CATALYST COMPOSITION THEREFOR ✓



(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, 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:—

The invention relates to a process for the catalytic incineration of hydrogen sulphide-containing waste gases by contacting said waste gases with a stoichiometric excess of oxygen with respect to the contained hydrogen sulphide in the presence of a catalyst. It also relates to a catalyst composition which can suitably be applied in such a process.

Viewed in the light of increasingly stringent requirements with respect to air pollution abatement, various procedures have been developed to remove hydrogen sulphide (H<sub>2</sub>S) from process off-gases, and even recover, if possible H<sub>2</sub>S or reaction products of H<sub>2</sub>S contained therein. For example, the well-known Claus process produces an effluent normally containing up to 2% or even 3% by weight sulphur compounds, a substantial proportion thereof being H<sub>2</sub>S.

To remove this concentration of sulphur compounds, selective absorption by contacting the Claus off-gases with a suitable absorption solvent, after, a hydrogenation treatment of the off-gases, has been practised. In this procedure, the bulk of the desorbed H<sub>2</sub>S after regeneration of the absorption solvent, is returned to the Claus unit, and the final off-gas or tail gas, containing nitrogen, CO<sub>2</sub> and quite minor amounts of H<sub>2</sub>S is incinerated. During incineration, H<sub>2</sub>S is converted to sulphur dioxide (SO<sub>2</sub>), a material which

generally has not been subjected to emission requirements as rigid as those applied to H<sub>2</sub>S. However, incineration is costly because of the necessary heat input. Again, although some work has been done with regard to catalytic conversion of H<sub>2</sub>S in the off-gas or tail gas to SO<sub>2</sub>, concomitant formation of sulfur trioxide (SO<sub>3</sub>) has been a problem.

A process is known for the purification of gases contaminated with hydrogen sulphide by oxidizing said hydrogen sulphide in the presence of catalysts which contain as the main constituents metals, such as nickel, iron, cobalt, manganese, zinc and copper, or their compounds, either alone or together with metals or metalloids of Groups 4, 5 and 6 of the Periodic System of Elements and in addition thereto, small quantities of an activating material, such as lead or bismuth or their compounds, or alkali metal or alkaline earth metal compounds. The amount of the activating material employed is up to about 10%, based on the weight of the total amount of metals present. Said known catalysts have a disadvantage in that their activity decreases rapidly, requiring a temperature raise of about 5°C every three days. Moreover, about 10% of the hydrogen sulphide, present is converted to SO<sub>3</sub>, which is a highly objectionable compound from an air pollution-abatement point of view.

Accordingly, there still exists a need for an economical method for the purification of H<sub>2</sub>S-containing streams, particularly off-gas streams of the type mentioned, which method would provide substantial conversion of the H<sub>2</sub>S values in the off-gas, and concomitantly provide low SO<sub>2</sub> emissions. The method should be economical in that the necessary heat input should be as low as possible as evidenced by relatively low process temperatures. Moreover, the catalysts to be applied should

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show an activity which remains constant over a long period.

The present invention has as its object to satisfy that need.

5 The present invention accordingly concerns a process for the catalytic incineration of hydrogen sulphide-containing waste gases by contacting said waste gases with a stoichiometric excess of oxygen with respect to the contained hydrogen sulphide in the presence of a catalyst in which process the hydrogen sulphide-containing waste gases are contacted with oxygen or an oxygen-containing gas at a temperature in the range of from 150° to 450°C in the presence of a catalyst comprising as the catalytically active components substantially only bismuth in an amount of from 0.6 to 10% by weight and copper in an amount of from 0.5 to 5% by weight, based on the total weight of the catalyst, bismuth being present in a major amount with respect to copper.

25 It has surprisingly been found that use of a catalyst containing both bismuth (Bi) and copper (Cu), in specified proportions and amounts, gives results not attainable by use of comparable amounts of Cu or Bi alone. The unexpected aspect of the process of the invention resides in the ability to utilize temperatures of reaction not attainable, on a weight basis, with catalysts of Cu or Bi alone. Additionally, any combustibles, e.g., H<sub>2</sub>, CO, CH<sub>4</sub>, present in the streams to be treated appear unaffected or substantially unaffected by the catalyst of the invention. The SO<sub>2</sub> formed may be vented or recovered in a manner known to those skilled in the art.

40 Although the invention is apparently applicable to any H<sub>2</sub>S-containing stream of low to moderate H<sub>2</sub>S concentration, the invention is ideally suited to the treatment of H<sub>2</sub>S containing off-gases from various processes from which no further or little recovery of other materials is made. The invention is eminently suited, as indicated, to the treatment of the effluent from a Claus plant. The Claus process is normally itself a "clean-up" process, wherein elemental sulphur is prepared by partial oxidation of H<sub>2</sub>S, using an oxygen-containing gas (including pure oxygen) to form SO<sub>2</sub>, followed by the reaction of SO<sub>2</sub> produced with the remaining part of the H<sub>2</sub>S in the presence of a catalyst. The process is frequently used at refineries and also for the work-up of H<sub>2</sub>S recovered from various gas streams, such as natural gas. Since the yield of elemental sulphur, relative to the hydrogen sulphide introduced, is not quantitative, a minor amount of unreacted H<sub>2</sub>S, COS, CS<sub>2</sub>, and SO<sub>2</sub> remains in the Claus off-gases. To some extent, the amount of elemental sulphur recovered depends on the number of

catalyst beds employed in the Claus process. In principle, about 98% of the total sulphur available can be recovered when three catalyst beds are used. The invention is eminently suited to the removal of H<sub>2</sub>S from Claus plant effluents.

70 Additionally, as indicated, Claus plant effluents or Claus off-gases may previously have been processed by a Claus tail gas treating process. Such a process may comprise the steps of reducing SO<sub>2</sub>, COS, CS<sub>2</sub>, and SO<sub>3</sub> contained in the gas under suitable conditions to H<sub>2</sub>S in the presence of a catalyst, absorbing the H<sub>2</sub>S followed by desorption of the H<sub>2</sub>S and recycle of the desorbed H<sub>2</sub>S to the Claus plant. Where this procedure is practised, the invention provides for the oxidation of the quite minor or reduced amounts of H<sub>2</sub>S, and the like, remaining in the final off-gas by contacting said off-gas with oxygen under the conditions indicated.

80 The catalyst employed in the process of the invention will be a solid material containing copper and bismuth as the catalytically active components. The particular form wherein the catalytically active components are present in the catalyst, i.e., whether as compounds or the elements or compounds combined in a carrier material, does not appear to be critical. Where a carrier is employed, the only apparent requirement concerning the sources of the copper and bismuth is that the copper and bismuth be in a form adapted to solution, either as an ordinary solution (both aqueous and organic solvents) or as a solution of a liquid or complex of copper or bismuth. Certain salts and the oxide and hydroxide of copper and bismuth may change during the preparation of the catalyst, during heating in a reactor prior to use in the process of this invention, or may be converted to another form under the described reaction conditions, but such materials still function as effective catalysts in the defined process. For example, the nitrates, nitrites, carbonates, hydroxides, citrates and acetates may be converted to the corresponding oxide and then to the sulphide under the reaction conditions defined herein. Such salts as the phosphate, sulphate, and halides, which are stable or partially stable at the defined reaction temperature, are similarly effective under the conditions of the described reaction, as well as such compounds which are converted to another stable form in the reactor. Copper nitrite and bismuth nitrate are, however, preferred materials, since they are inexpensive and are readily soluble in water and can easily be deposited on carriers. The catalysts of this invention are solid at room temperature or are essentially

solid under the conditions of reaction (although some volatilization may occur).

To achieve meaningful lowering of the reaction temperature with concomitant COS conversion the presence of minimum amounts of Cu and Bi is essential. In general, concentrations of at least 0.5% Cu and 0.6% Bi (all by weight) are required in the reaction zone, with concentrations of at least 0.8% Bi being preferred. Dramatic improvement over the Cu and Bi alone occurs when the concentration of Cu is at least about 1.0% and the concentration of Bi is at least about 2.0% (all by weight). Where a carrier is employed, for example, the Cu will normally be present in an amount of up to 5% by weight, based on the total weight of the catalyst material. Preferably, the amount of Cu will not exceed 3% by weight and the amount of Bi, preferably, does not exceed 5% by weight. However, the amount of bismuth present in the catalyst is always such that the catalyst comprises a major amount of bismuth and a minor amount of copper.

If solid compounds of Cu and Bi are employed, or if heavy concentrations of Cu and Bi on a carrier are employed, the catalytically active materials will normally be diluted with inert materials so that activity may be regulated. Proper dilution to the concentrations specified is within the skill of the art, and need not be detailed herein.

Excellent results have been obtained by packing the reactor with the defined catalyst particles as the method of introducing the catalytic surface. The size of the catalyst particles may vary widely, but generally the maximum particle size will at least pass through a Tyler standard screen which has an opening of 2 inches, and the largest particles of catalyst will pass through a Tyler screen with one inch openings. Very small particle size carriers may be utilized, the only practical objection being that extremely small particles cause excessive pressure drops across the reactor. In order to avoid high pressure drops across the reactor, at least 50% by weight of the catalyst should be retained by a 4 to 5 mesh Tyler standard screen. However, if a fluid bed reactor is utilized, catalyst particles may be quite small, such as from about 10 to 300 microns. Those skilled in the art can readily determine appropriate particle size depending on reactor configuration and size, and gas velocity to be applied.

If a carrier is used, the catalytically active components may be deposited on the carrier by methods known in the art, such as by preparing in aqueous solution or dispersion of the described catalyst, and mixing the carrier particles with the solution or dispersion until the active ingredients are

deposited in or on the carrier. The coated particles may then be dried, for example, in an oven at about 110°C. Various other methods of catalyst preparation known to those skilled in the art may be used. Very useful carriers (and dilutants) are fused aluminas (Alundum),\* silica, silicon carbide (Carborundum), pumice, kieselguhr, asbestos, and zeolites. The fused aluminas or other alumina carriers and silica are particularly preferred. The carriers may be of any shape, including irregular shapes.

Another method for introducing the required surface is to utilize as a reactor a small diameter tube wherein the tube wall is catalytic or is coated with catalytic material. If the tube wall is the only source of catalyst, the tube wall will generally be of an internal diameter of no greater than one inch, such as less than 3/4 inch in diameter, or preferably will be no greater than about 1/2 inch in diameter. Other methods may be utilized to introduce the catalytic surface. For example, the technique of a fluidized bed may be used.

The concentration of H<sub>2</sub>S in the streams treated may vary widely. Thus, the concentrations may range from trace quantities to quite significant amounts, and it will be recognized by those skilled in the art that H<sub>2</sub>S concentrations are not generally a limiting factor of the invention. For example, concentrations of H<sub>2</sub>S in the gases treated may range from 0.005% to 5.0%, or even 10.0% (molar basis). Concentrations of COS and CS<sub>2</sub> present in Claus effluents are normally also minor, and will range for example from about 0.01% to about 0.5% (molar basis).

Reaction conditions employed may vary considerably. While the temperatures at which the reaction is carried out are not critical, it is an advantage of the invention that lower or more moderate temperatures may be employed. Temperatures of 150°C to 450°C are quite satisfactory, while temperatures of 250°C to 420°C are preferred.

Similarly, the pressures employed are not critical, and a wide range of pressures may be used. For example, the total pressure in the system of the invention normally will be at or in excess of atmospheric pressure, although in some embodiments a partial vacuum may be used. Preferably, pressures will range from atmospheric to higher pressures, such as 5 or even 10 atmospheres. Steam may be present in the system, and in some instances, is preferred.

The flow rates of the H<sub>2</sub>S-containing gas and the oxygen are largely a matter of choice. However, as will be recognized by

\*("Alundum" is a registered Trade Mark).

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those skilled in the art, lower space velocities improve conversion levels. Generally, gaseous flow rates of from 1,000 GHSV to 50,000 GHSV may be used, with rates of from 2,000 GHSV to 25,000 GHSV being preferred. Good results have been obtained with space velocities of 2,000 to 10,000 GHSV. Contact times, accordingly, are widely variable, and may range from 0.07 seconds to 4.0 seconds, with contact times of from 0.14 seconds to 2.0 seconds being preferred.

The amount of oxygen supplied to the reaction zone is important, in that a stoichiometric excess, preferably a large excess, of oxygen is desired in order to react all the  $H_2S$  and any  $COS$  and  $CS_2$  present. In general, at least twice, and normally up to five times the stoichiometric amount of oxygen required for the reaction may be supplied. Preferably, an excess of 20 to 280% of the stoichiometric amount of oxygen, based upon all total combustibles, will be supplied. Amounts as high as 100 or even 200 times the stoichiometric amount of oxygen may be supplied, if desired. The oxygen may be supplied as relatively pure oxygen, as air, or mixtures of air and oxygen, as well as from other gaseous streams containing significant quantities of oxygen and other components which do not interfere significantly with the reaction contemplated.

#### EXAMPLE I

In order to demonstrate the invention, the following experiments were conducted. In each run, a synthetic tail gas containing  $H_2S$  and other sulphur compounds is passed into a reactor containing the catalyst. Oxygen, as air, is introduced from a separate line. Temperature is measured by suitable means, and conversion results are obtained by analysis of the effluent stream from the reactor.

Employing this general procedure, samples were taken employing a catalyst containing Bi and Cu deposited on alumina (Kaiser A-201 spherical gamma-alumina, 4x6 mesh) in amounts of 3% and 1% respectively, each by weight, based on the total weight of the catalyst. Copper and bismuth were deposited as a basic solution of the nitrates. The catalyst was then dried and calcined at 481°C for one to two hours before use. Conditions of operation are shown more specifically in Table I.

Significant  $H_2S$ -removal is obtained, and the results for two different space velocities are shown in Table II.

TABLE I

| Composition, %v |           |
|-----------------|-----------|
| $H_2S$          | 0.8       |
| $SO_2$          | 0.4       |
| $S_2$           | 0.15      |
| $COS$           | 0.04      |
| $CS_2$          | 0.04      |
| $CO_2$          | 5.00      |
| $CO$            | 0.50      |
| $H_2$           | 1.00      |
| $H_2O$          | 30.00     |
| Air             | variable  |
| $N_2$           | remainder |

#### Operating Conditions

|                 |                                                    |
|-----------------|----------------------------------------------------|
| Pressure:       | 1 atmosphere                                       |
| Temperature:    | 290°—425°C                                         |
| Space velocity: | 2500 to 5000 vol./vol./h<br>(basis reactor outlet) |
| Air rate:       | 20—280% excess $O_2$ *)                            |

\*) Based upon all total combustibles, including hydrogen.

TABLE II

| Catalyst                    | 1% Cu—3% Bi/ $Al_2O_3$ |      |
|-----------------------------|------------------------|------|
| Space velocity, vol./vol./h | 2500                   | 5000 |
| Temperature, °C             | 370                    | 370  |
| Excess $O_2$ , %            | 150                    | 150  |

#### Wet chemical analysis

| Product gas (dry basis) |      |
|-------------------------|------|
| $H_2S$ , ppmv           | 0.1  |
| $SO_2$ , %v             | 2.23 |
| $SO_3$ , ppmv           | 6    |

#### EXAMPLE II

Employing a procedure similar to Example I, a catalyst containing only 3% by weight (based on the weight of the active material and carrier) bismuth on alumina and a catalyst containing only 1% by weight (based on the weight of the active material and carrier) copper on alumina were prepared and tested. Results are shown in Table III and compared with those for a catalyst in accordance with the invention.

TABLE III  
Comparison of catalyst compositions

|    | Catalyst                       | 3% Bi/Al <sub>2</sub> O <sub>3</sub> | 1% Cu/Al <sub>2</sub> O <sub>3</sub> | 1% Cu—3%<br>Bi/Al <sub>2</sub> O <sub>3</sub> |
|----|--------------------------------|--------------------------------------|--------------------------------------|-----------------------------------------------|
| 5  | Space velocity,<br>vol./vol./h | —                                    | 2500                                 | —                                             |
|    | Temperature °C                 | —                                    | 315                                  | —                                             |
|    | Excess O <sub>2</sub> , %      | —                                    | 150                                  | —                                             |
|    | Wet chemical analysis          |                                      |                                      |                                               |
| 10 | Product gas (dry<br>basis)     |                                      |                                      |                                               |
|    | H <sub>2</sub> S, vpmv         | 2.1                                  | 0.1                                  | 0.14                                          |
|    | SO <sub>2</sub> , %v           | 2.18                                 | 2.04                                 | 2.10                                          |
|    | SO <sub>3</sub> , ppmv         | 22                                   | 71                                   | 8                                             |

The data in Table III demonstrate clearly the superiority of the Cu—Bi catalyst with respect to the reduced SO<sub>3</sub>-concentration in the product gas. The combination catalyst in accordance with the invention also shows a very high conversion for carbonyl sulphide and carbon disulphide. At the reaction conditions specified the carbonyl sulphide conversion is better than 50% and the carbon disulphide conversion is better than 90%.

#### WHAT WE CLAIM IS:—

1. A process for the catalytic incineration of hydrogen sulphide-containing waste gases by contacting said waste gases with a stoichiometric excess of oxygen with respect to the contained hydrogen sulphide in the presence of a catalyst, in which the hydrogen sulphide-containing waste gases are contacted with oxygen or an oxygen-containing gas at a temperature in the range of from 150 to 450°C in the presence of a catalyst comprising as the catalytically active components substantially only bismuth in an amount of from 0.6 to 10% by weight and copper in an amount of from 0.5 to 5% by weight, based on the total weight of the catalyst, bismuth being present in a major amount with respect to copper.

2. A process as claimed in Claim 1, wherein the catalyst comprises of from 0.8 to 5% by weight of bismuth and of from 0.5 to 3% by weight of copper.

3. A process as claimed in Claim 1 or Claim 2 wherein the oxygen is supplied in an amount of up to 5 times the stoichiometric amount of oxygen required.

4. A process as claimed in Claim 3, in which the oxygen is supplied in an excess of 20% to 280% of the stoichiometric amount of oxygen.

5. A process as claimed in any one of

Claims 1 to 4, wherein the hydrogen sulphide-containing waste gas is a Claus off-gas.

6. A process as claimed in any one of Claims 1 to 4, wherein the hydrogen sulphide-containing waste gas is an off-gas of a Claus tail gas-treating process.

7. A process as claimed in any one of Claims 1 to 6, wherein the hydrogen sulphide-containing waste gas comprises from 0.005 up to 5.0% mol. H<sub>2</sub>S.

8. A process as claimed in any one of Claims 1 to 7, wherein the temperature is from 250°C to 420°C.

9. A process as claimed in Claim 1, substantially as described hereinbefore with reference to the Examples.

10. A catalyst composition comprising a carrier material and substantially only copper and bismuth as the catalytically active components, copper being present in a minor amount of from 0.5 to 5% by weight and bismuth in a major amount of from 0.6 to 10% by weight, based on the total weight of the catalyst composition.

11. A catalyst composition as claimed in Claim 10, wherein the carrier material is chosen from the group comprising fused aluminas, silica and alumina.

12. A catalyst composition as claimed in Claim 10 or Claim 11, comprising 0.5 to 3.0% by weight of copper and 0.8 to 5.0% by weight of bismuth, the carrier material being alumina, preferably gamma-alumina.

13. A catalyst composition as claimed in Claim 10, substantially as described hereinbefore with reference to the Examples.

R. C. ROGERS,  
Chartered Patent Agent,  
Shell Centre,  
London, SE1 7NA  
Agent for the Applicants.

TABLE III  
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| Catalyst                    | 3% Bi/Al <sub>2</sub> O <sub>3</sub> | 1% Cu/Al <sub>2</sub> O <sub>3</sub> | 1% Cu—3% Bi/Al <sub>2</sub> O <sub>3</sub> |
|-----------------------------|--------------------------------------|--------------------------------------|--------------------------------------------|
| Space velocity, vol./vol./h | —                                    | 2500                                 | —                                          |
| Temperature °C              | —                                    | 315                                  | —                                          |
| Excess O <sub>2</sub> , %   | —                                    | 150                                  | —                                          |

Wet chemical analysis

Product gas (dry basis)

|                        |      |      |      |
|------------------------|------|------|------|
| H <sub>2</sub> S, vpmv | 2.1  | 0.1  | 0.14 |
| SO <sub>2</sub> , %v   | 2.18 | 2.04 | 2.10 |
| SO <sub>3</sub> , ppmv | 22   | 71   | 8    |

The data in Table III demonstrate clearly the superiority of the Cu—Bi catalyst with respect to the reduced SO<sub>3</sub>-concentration in the product gas. The combination catalyst in accordance with the invention also shows a very high conversion for carbonyl sulphide and carbon disulphide. At the reaction conditions specified the carbonyl sulphide conversion is better than 50% and the carbon disulphide conversion is better than 90%.

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1. A process for the catalytic incineration of hydrogen sulphide-containing waste gases by contacting said waste gases with a stoichiometric excess of oxygen with respect to the contained hydrogen sulphide in the presence of a catalyst, in which the hydrogen sulphide-containing waste gases are contacted with oxygen or an oxygen-containing gas at a temperature in the range of from 150 to 450°C in the presence of a catalyst comprising as the catalytically active components substantially only bismuth in an amount of from 0.6 to 10% by weight and copper in an amount of from 0.5 to 5% by weight, based on the total weight of the catalyst, bismuth being present in a major amount with respect to copper.

2. A process as claimed in Claim 1, wherein the catalyst comprises of from 0.8 to 5% by weight of bismuth and of from 0.5 to 3% by weight of copper.

3. A process as claimed in Claim 1 or Claim 2 wherein the oxygen is supplied in an amount of up to 5 times the stoichiometric amount of oxygen required.

4. A process as claimed in Claim 3, in which the oxygen is supplied in an excess of 20% to 280% of the stoichiometric amount of oxygen.

5. A process as claimed in any one of

Claims 1 to 4, wherein the hydrogen sulphide-containing waste gas is a Claus off-gas.

6. A process as claimed in any one of Claims 1 to 4, wherein the hydrogen sulphide-containing waste gas is an off-gas of a Claus tail gas-treating process.

7. A process as claimed in any one of Claims 1 to 6, wherein the hydrogen sulphide-containing waste gas comprises from 0.005 up to 5.0% mol. H<sub>2</sub>S.

8. A process as claimed in any one of Claims 1 to 7, wherein the temperature is from 250°C to 420°C.

9. A process as claimed in Claim 1, substantially as described hereinbefore with reference to the Examples.

10. A catalyst composition comprising a carrier material and substantially only copper and bismuth as the catalytically active components, copper being present in a minor amount of from 0.5 to 5% by weight and bismuth in a major amount of from 0.6 to 10% by weight, based on the total weight of the catalyst composition.

11. A catalyst composition as claimed in Claim 10, wherein the carrier material is chosen from the group comprising fused aluminas, silica and alumina.

12. A catalyst composition as claimed in Claim 10 or Claim 11, comprising 0.5 to 3.0% by weight of copper and 0.8 to 5.0% by weight of bismuth, the carrier material being alumina, preferably gamma-alumina.

13. A catalyst composition as claimed in Claim 10, substantially as described hereinbefore with reference to the Examples.

R. C. ROGERS,  
Chartered Patent Agent.  
Shell Centre,  
London, SE1 7NA  
Agent for the Applicants.

