

# PATENT SPECIFICATION

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NO DRAWINGS.

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## COMPLETE SPECIFICATION.

### Process for the Regeneration of Solid Sulphur Dioxide Acceptors.

We, SHELL INTERNATIONALE RESEARCH  
MAATSCHAPPIJ N.V., a company organised  
under the laws of The Netherlands, of 30  
Carel van Bylandtlaan, The Hague, The  
Netherlands, do hereby declare the inven-  
tion, 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 de-  
scribed in and by the following statement:—

The invention relates to a process for the  
regeneration of a sulphur dioxide-loaded ac-  
ceptor obtained by contacting a gas mixture  
comprising one or more sulphur oxides and  
oxygen with a solid acceptor comprising a  
solid carrier material composited with a  
metal and/or a metal compound capable of  
taking up sulphur oxides to form a metal  
sulphate. The invention further relates to a  
process for the preparation of a metal and/  
or a metal oxide composited with a refrac-  
tory carrier material.

It is known to composite a metal and/or  
a metal oxide with a refractory carrier ma-  
terial—this composition is also named here-  
inafter "acceptor"—to remove sulphur  
oxides from gas mixtures. Sulphur oxide re-  
moval, in particular from hot waste gases  
having a relatively low sulphur content—  
such as flue gases and gases originating from  
roasting processes—has in the past few years  
become a technical problem. The application  
of a copper-comprising acceptor is attractive  
as it may be used at flue gas temperatures,  
that is to say at 200—500°C. During contact  
with the acceptor sulphur dioxide and/or  
trioxide is (are) accepted by the copper and/  
or copper oxide so that the purified gases, if  
discharged via a stack, cause substantially no  
air pollution. The copper sulphate formed

during acceptance may subsequently be de-  
composed by means of a reducing gas, the  
result being a regenerated acceptor and a gas  
considerably richer in sulphur dioxide than  
the flue gas. The regenerated acceptor may  
be used to purify a further quantity of gas  
comprising sulphur oxides. Said sulphur di-  
oxide-rich gas may be used for any suitable  
purpose, for example, to produce elemental  
sulphur or sulphuric acid. Another attractive  
feature of this acceptor is that acceptance  
and regeneration may be carried out at sub-  
stantially the same temperature, cooling or  
heating of the acceptor between acceptance  
and regeneration not being necessary.

The regeneration may be carried out with  
the aid of hydrocarbons, which compounds  
have the attractive feature of a high regen-  
eration rate. It may, however, occur that  
during regeneration with hydrocarbons com-  
bustible material is deposited on the accep-  
tor. This may be an inconvenience as the  
oxygen present in the gas mixture causes  
burning of the combustible material during  
the acceptance step following such a regenera-  
tion and the heat of combustion then liber-  
ated causes a temperature increase of the  
acceptor particles. This temperature increase  
is undesirable in that it may have an un-  
favourable effect on the crushing strength of  
the particles and, consequently, on the ac-  
ceptor life. The higher the molecular weight  
of the hydrocarbons, the more combustible  
material is deposited. Relatively large quan-  
tities of combustible material are deposited  
when saturated hydrocarbons having more  
than four carbon atoms per molecule and  
unsaturated hydrocarbons are used for re-  
generation. Burning these large quantities

[Price 5s. 0d.]

causes a particularly high temperature increase of the acceptor particles, resulting in a relatively short acceptor life.

5 It is an object of the invention to provide a process in which only minor quantities of combustible material are deposited on the acceptor. Another object is to provide a process in which hydrocarbons are easily recovered from spent regeneration gas.

10 The present invention accordingly provides a process for the regeneration of a sulphur dioxide-loaded acceptor obtained by contacting a gas mixture comprising one or more sulphur oxides and oxygen with a solid acceptor comprising a solid refractory carrier material composited with a metal and/or a metal compound capable of taking up sulphur oxides to form a metal sulphate, which process comprises treating said loaded acceptor with a reducing gas comprising one or more hydrocarbons and an inert diluent and removing spent gas comprising sulphur dioxide.

25 The reducing gas must comprise a diluent because it has been found advantageous that the hydrocarbon partial pressure is decreased. An acceptor regenerated with the aid of a dilute gas comprises appreciably less deposited combustible material than an acceptor regenerated with the aid of an undiluted hydrocarbon. This finding is of considerable importance, because the above-mentioned temperature increase during acceptance is correspondingly smaller and, consequently, acceptor life is longer. An attractive feature of the process of the invention is, moreover, that the diluent has substantially no influence on the hydrocarbon amount required for complete regeneration, the sulphur dioxide content of the spent gas (without taking into account the diluent) being substantially equal to that of a diluent-free spent gas obtained under the same conditions.

45 As explained hereinbefore, the metal and/or metal compound used preferably is (are) copper and/or copper oxide. Another acceptor having the same advantages as the copper-containing acceptor is one of which the solid refractory carrier material used is composited with a vanadium compound and an alkali metal compound capable to take up sulphur oxides. Examples of the latter compounds are alkali metal oxides, carbonates and hydroxides.

60 The volume ratio between the diluent and the hydrocarbons may vary within a wide range. This ratio may be very small, for example 0.2:1 or very large, for example 20:1. Preferably the reducing gas used comprises said inert diluent and hydrocarbon or hydrocarbons in a volume ratio in the range of from 10:1 to 0.5:1 and particularly in the range of from 6:1 to 1:1.

65 The diluent must be inert. This means

that the diluent itself should be unable to convert copper sulphate into copper or copper oxide. Examples of inert diluents are steam, carbon dioxide and nitrogen. The use of steam deserves preference, it being very active in suppressing deposition of combustible material. An attractive feature of steam is, moreover, the fact that it condenses when a spent sulphur dioxide-comprising gas is cooled to ambient temperature.

70 The higher the molecular weight of hydrocarbons the more is their activity as reducing agents. Methane and ethane may be used, but it is preferred to employ a reducing gas comprising one or more hydrocarbons with at least three carbon atoms per molecule. For example, gases comprising propane and/or a butane may be used. Reduction is still more rapid if the reducing gas comprises one or more hydrocarbons with at least five carbon atoms per molecule and hydrocarbons having a boiling point at atmospheric pressure in the range of from 40° to 200°C are particularly attractive in this respect. Hydrocarbons having a boiling point at atmospheric pressure higher than 200°C may be used as well.

75 The spent gas comprises mainly sulphur dioxide, carbon dioxide, water, hydrocarbons and inert diluent. Hydrocarbons recovered from said spent gas comprising sulphur dioxide are preferably reused in the process. In the latter embodiment of the present process, efficient hydrocarbon use combines with the production of a gas still richer in sulphur dioxide. Hydrocarbon recovery may, for example, be carried out with the aid of a solvent which physically dissolves sulphur dioxide and carbon dioxide, for example with cyclotetramethylene sulphone when light hydrocarbons such as methane, ethane, propane and/or butane are present. Another attractive feature of hydrocarbons having a boiling point at atmospheric pressure in the range of from 40° to 200°C is that they may easily be removed from a spent gas, no solvent being required. This simple removal may take place by means of condensation. Therefore, when the reducing gas comprises one or more hydrocarbons with at least five carbon atoms per molecule, said spent gas comprising sulphur dioxide is preferably cooled until a hydrocarbon condensate is formed, which condensate, after evaporation, is re-used in the process. For example, when a spent gas comprising hydrocarbons boiling in the range between 100° and 200°C is cooled to 50°C, a very large part of these hydrocarbons (and steam) is condensed, leaving a gas very rich in sulphur dioxide. This spent gas may be cooled at atmospheric pressure. Hydrocarbons having less than five carbon atoms per molecule may also be removed by condensing them, but this

requires a pressure higher than atmospheric.

The carrier material must be refractory and may for example comprise an alumina-comprising refractory oxide. As examples of suitable carrier materials may be mentioned bauxite, synthetic alumina, silica-alumina and/or natural clays, whether or not pretreated with acid. A very suitable carrier material is  $\gamma$ -alumina. Other examples of carrier materials are silica and silica-magnesia.

The metal content of the acceptor may vary within wide limits. The acceptor preferably comprises from 5 to 15% by weight of said metal, calculated as metal on carrier material.

The temperature at which the copper sulphate is reduced may vary within a wide range. Preferably, the loaded acceptor is treated at a temperature in the range of from 200° to 500°C and particularly in the range of from 350° to 450°C. For example, the reducing gas may comprise n-octane and a temperature of 370°C may be used.

As stated hereinbefore, the metal compound to be reduced has been formed by acceptance of sulphur oxides. However, the metal compound may have been formed in any suitable way. For example, the carrier material may have been impregnated with an aqueous solution comprising copper sulphate, followed by drying and calcining of the impregnated material. Therefore, the present invention also relates to a process for the preparation of a metal and/or metal oxide composited with a refractory carrier material, which process comprises reducing

a metal sulphate present on said carrier material with a gas comprising one or more hydrocarbons and an inert diluent. The metal and/or metal oxide thus prepared may be used for any suitable purpose, for example as an oxidation catalyst.

The process of the invention will further be illustrated with the aid of the following Examples.

#### EXAMPLE I

A reactor comprising a number of thin and parallel acceptor layers, each layer having a length of 500 cm was charged with 71.1 kg (114.5 l) of an acceptor comprising metallic copper (9%w copper calculated on alumina) on  $\gamma$ -alumina. The acceptor was loaded by conducting a flue gas comprising 2.9%w sulphur dioxide at a temperature of 425°C and a gas hourly space velocity of 5200 Nm<sup>3</sup>/m<sup>3</sup>/h through the gas channels present between the acceptor layers. Then, the loaded acceptor was regenerated at 425°C at a gas hourly space velocity of 28 Nm<sup>3</sup> butane/m<sup>3</sup>/h. In a first experiment, the loaded acceptor was regenerated with a gas consisting of n-butane and the acceptor thus regenerated again loaded with sulphur dioxide as described above. In a second experiment the loaded acceptor was regenerated with a mixture consisting of equal molar quantities of n-butane and steam. Subsequently, the regenerated acceptor was again loaded with sulphur dioxide as described above. Table I shows the temperature increase after the start of the load-up at three places in the reactor.

TABLE I

| Distance from reaction inlet, m | Temperature increase during load-up, °C after regeneration with |                |
|---------------------------------|-----------------------------------------------------------------|----------------|
|                                 | n-butane                                                        | diluted butane |
| 3                               | 147                                                             | 60             |
| 4                               | 153                                                             | 81             |
| 5                               | 160                                                             | 57             |

Some data on the sulphur dioxide content of the spent regeneration gas at various times after the start of the regeneration are presented in Table II.

TABLE II

|                                        |    | SO <sub>2</sub> content of spent regeneration gas,<br>%v when regenerating with |                |
|----------------------------------------|----|---------------------------------------------------------------------------------|----------------|
|                                        |    | n-butane                                                                        | diluted butane |
| after minutes of start of regeneration |    |                                                                                 |                |
| 5                                      | 5  | 36.5                                                                            | 34.5           |
|                                        | 10 | 20.5                                                                            | 22.5           |
|                                        | 20 | 9.5                                                                             | 4.5            |
|                                        | 40 | 3.5                                                                             | 0.5            |

The sulphur dioxide contents have been calculated without taking into account the steam added to the n-butane. The results collected in Table II show that at a given time after the start of regeneration the sulphur dioxide contents of the spent regeneration gases are substantially the same.

## EXAMPLE II

The experiments described in Example I were repeated, the difference being that the loaded acceptor was regenerated with a light gasoline fraction boiling between 40 and

100°C. In one experiment the loaded acceptor was regenerated with the gasoline fraction as such as a gas hourly space velocity of 16 Nm<sup>3</sup>/m<sup>3</sup>/h. In another experiment the loaded acceptor was regenerated with a mixture consisting of 21.7%v gasoline, 41.3%v steam and 37.0%v nitrogen at a gas hourly space velocity of 20 Nm<sup>3</sup> gasoline/m<sup>3</sup>/h. Table III shows the temperature increase after the start of the next sulphur dioxide load-up at four places in the reactor.

TABLE III

|                                |   | Temperature increase during load-up,<br>°C after regeneration with |                  |
|--------------------------------|---|--------------------------------------------------------------------|------------------|
|                                |   | undiluted gasoline                                                 | diluted gasoline |
| distance from reactor inlet, m |   |                                                                    |                  |
| 35                             | 2 | 114                                                                | 32               |
|                                | 3 | 156                                                                | 54               |
|                                | 4 | 184                                                                | 72               |
|                                | 5 | 172                                                                | 86               |

## EXAMPLE III

The acceptor present in the reactor described in Example I was loaded and then regenerated with the aid of a gasoline fraction boiling between 60 and 80°C, and

diluted with a mixture of equal molar quantities of nitrogen and steam. The results of three of these experiments are given in Table IV.

TABLE IV

|                                   |   | temperature increase during load-up, °C, after regeneration with |                                                                       |     |     |
|-----------------------------------|---|------------------------------------------------------------------|-----------------------------------------------------------------------|-----|-----|
| distance from<br>reactor inlet, m |   | undiluted gasoline                                               | diluted gasoline, volume ratio between<br>diluent and gasoline vapour |     |     |
|                                   |   |                                                                  | 2.5                                                                   | 3.6 | 5.5 |
| 55                                | 2 | 144                                                              | 48                                                                    | 36  | 36  |
|                                   | 3 | 156                                                              | 77                                                                    | 55  | 36  |
|                                   | 4 | 184                                                              | 110                                                                   | 74  | 50  |
|                                   | 5 | 172                                                              | 104                                                                   | 84  | 56  |

The space velocities during regeneration were 18, 20 and 8 Nm<sup>3</sup> of gasoline vapour/m<sup>3</sup> acceptor/hour, relating to the volume ratios 2.5, 3.6 and 5.5, respectively.

#### 5 EXAMPLE IV

The acceptor present in the reactor de-

scribed in Example I was loaded and then regenerated with the aid of a gasoline fraction boiling between 100° and 160°C, diluted with steam. The results of two ex- 10  
periments are presented in Table V.

TABLE V

| 15 | distance from reactor inlet, m | temperature increase during load-up,<br>°C, at a volume ratio between steam<br>and gasoline vapour of |     |
|----|--------------------------------|-------------------------------------------------------------------------------------------------------|-----|
|    |                                | 3.5                                                                                                   | 8.8 |
| 20 | 2                              | 112                                                                                                   | 44  |
|    | 3                              | 103                                                                                                   | 52  |
|    | 4                              | 171                                                                                                   | 82  |
|    | 5                              | 151                                                                                                   | 44  |

The space velocity of the regeneration relating to the middle column was 16.7 and that to the right-hand column of Table V was 6.6 Nm<sup>3</sup> gasoline vapour/m<sup>3</sup> acceptor/hour.

#### WHAT WE CLAIM IS:—

1. Process for the regeneration of a sulphur-dioxide-loaded acceptor obtained by contacting a gas mixture comprising one or more sulphur oxides and oxygen with a solid acceptor comprising a solid refractory carrier material composited with a metal and/or a metal compound capable of taking up sulphur oxides to form a metal sulphate, which process comprises treating said loaded acceptor with a reducing gas comprising one or more hydrocarbons and an inert diluent and removing a spent gas comprising sulphur dioxide.

2. Process as claimed in claim 1, in which the metal and/or metal compound used is (are) copper and/or copper oxide.

3. Process as claimed in claim 1, in which said solid carrier material used is composited with a vanadium compound and an alkali metal compound capable to take up sulphur oxides.

4. Process as claimed in any one of the preceding claims, in which the reducing gas used comprises said inert diluent and hydrocarbon, or hydrocarbons, in a volume ratio in the range of from 10:1 to 0.5:1.

5. Process as claimed in any one of the preceding claims, in which the reducing gas used comprises said inert diluent and hydrocarbon, or hydrocarbons, in a volume ratio in the range of from 6:1 to 1:1.

6. Process as claimed in any one of the preceding claims, in which said inert diluent is steam.

7. Process as claimed in any one of the preceding claims, in which the reducing gas comprises one or more hydrocarbons with at least three carbon atoms per molecule.

8. Process as claimed in any one of the preceding claims, in which the reducing gas comprises one or more hydrocarbons with at least five carbon atoms per molecule.

9. Process as claimed in any one of the preceding claims, in which the reducing gas comprises hydrocarbons having a boiling point at atmospheric pressure in the range of from 40 to 200°C.

10. A process as claimed in any one of the preceding claims, in which hydrocarbons recovered from spent gas comprising said sulphur dioxide, are re-used in the process.

11. A process as claimed in any one of the preceding claims, in which said spent gas comprising sulphur dioxide is cooled until a hydrocarbon condensate is formed, which condensate after evaporation, is re-used in the process, a pressure greater than atmospheric being used in the cooling when the hydrocarbon condensate will not condense by cooling at atmospheric pressure.

12. Process as claimed in any one of the preceding claims, in which the loaded acceptor is treated at a temperature in the range of from 200 to 500°C.

13. Process as claimed in any one of the preceding claims, in which the loaded acceptor is treated at a temperature in the range of from 350° to 450°C.

14. Process as claimed in any one of the preceding claims, in which the acceptor comprises from 5 to 15%w of said metal, calculated as metal on carrier material.

15. Process as claimed in any one of the preceding claims, in which the carrier material is  $\gamma$ -alumina.

The space velocities during regeneration were 18, 20 and 8 Nm<sup>3</sup> of gasoline vapour/m<sup>3</sup> acceptor/hour, relating to the volume ratios 2.5, 3.6 and 5.5, respectively.

#### EXAMPLE IV

The acceptor present in the reactor de-

scribed in Example I was loaded and then regenerated with the aid of a gasoline fraction boiling between 100° and 160°C, diluted with steam. The results of two ex-

TABLE V

| distance from reactor inlet, m | temperature increase during load-up,<br>°C, at a volume ratio between steam<br>and gasoline vapour of |     |
|--------------------------------|-------------------------------------------------------------------------------------------------------|-----|
|                                | 3.5                                                                                                   | 8.8 |
| 2                              | 112                                                                                                   | 44  |
| 3                              | 103                                                                                                   | 52  |
| 4                              | 171                                                                                                   | 82  |
| 5                              | 151                                                                                                   | 44  |

The space velocity of the regeneration relating to the middle column was 16.7 and that to the right-hand column of Table V was 6.6 Nm<sup>3</sup> gasoline vapour/m<sup>3</sup> acceptor/hour.

#### WHAT WE CLAIM IS:—

1. Process for the regeneration of a sulphur-dioxide-loaded acceptor obtained by contacting a gas mixture comprising one or more sulphur oxides and oxygen with a solid acceptor comprising a solid refractory carrier material composited with a metal and/or a metal compound capable of taking up sulphur oxides to form a metal sulphate, which process comprises treating said loaded acceptor with a reducing gas comprising one or more hydrocarbons and an inert diluent and removing a spent gas comprising sulphur dioxide.

2. Process as claimed in claim 1, in which the metal and/or metal compound used is (are) copper and/or copper oxide.

3. Process as claimed in claim 1, in which said solid carrier material used is composited with a vanadium compound and an alkali metal compound capable of taking up sulphur oxides.

4. Process as claimed in any one of the preceding claims, in which the reducing gas used comprises said inert diluent and hydrocarbon, or hydrocarbons, in a volume ratio in the range of from 10:1 to 0.5:1.

5. Process as claimed in any one of the preceding claims, in which the reducing gas used comprises said inert diluent and hydrocarbon, or hydrocarbons, in a volume ratio in the range of from 6:1 to 1:1.

6. Process as claimed in any one of the preceding claims, in which said inert diluent is steam.

7. Process as claimed in any one of the preceding claims, in which the reducing gas comprises one or more hydrocarbons with at least three carbon atoms per molecule.

8. Process as claimed in any one of the preceding claims, in which the reducing gas comprises one or more hydrocarbons with at least five carbon atoms per molecule.

9. Process as claimed in any one of the preceding claims, in which the reducing gas comprises hydrocarbons having a boiling point at atmospheric pressure in the range of from 40 to 200°C.

10. A process as claimed in any one of the preceding claims, in which hydrocarbons recovered from spent gas comprising said sulphur dioxide, are re-used in the process.

11. A process as claimed in any one of the preceding claims, in which said spent gas comprising sulphur dioxide is cooled until a hydrocarbon condensate is formed, which condensate after evaporation, is re-used in the process, a pressure greater than atmospheric being used in the cooling when the hydrocarbon condensate will not condense by cooling at atmospheric pressure.

12. Process as claimed in any one of the preceding claims, in which the loaded acceptor is treated at a temperature in the range of from 200 to 500°C.

13. Process as claimed in any one of the preceding claims, in which the loaded acceptor is treated at a temperature in the range of from 350° to 450°C.

14. Process as claimed in any one of the preceding claims, in which the acceptor comprises from 5 to 15%w of said metal, calculated as metal on carrier material.

15. Process as claimed in any one of the preceding claims, in which the carrier material is  $\gamma$ -alumina.



16. Process as claimed in any one of the preceding claims, in which said gas mixture is a flue gas.
17. Process as claimed in any one of the preceding claims, substantially as hereinbefore described.
18. Process as claimed in any one of the preceding claims, with reference to either of the Examples.
19. A solid acceptor comprising a solid carrier material composited with a metal and/or a metal oxide, whenever regenerated with the aid of a process as claimed in any one of the preceding claims.
20. A spent gas comprising sulphur dioxide, whenever removed with the aid of a process as claimed in any one of claims 1 to 18.
21. Process for the preparation of a metal and/or metal oxide composited with a refractory carrier material, which process comprises reducing a metal sulphate present on said carrier material with a gas comprising one or more hydrocarbons and an inert diluent.
22. A metal and/or metal oxide composited with a refractory carrier material, whenever prepared with the aid of a process as claimed in claim 21.

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