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1154009

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for the Removal of Sulphur Oxides from Gas Mixtures

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 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 removing sulphur oxides from a free oxygen-containing gas mixture by contacting the said mixture with a solid acceptor.

As a consequence of increasing industrialization the prevention of air pollution is receiving more and more attention. The removal of sulphur oxides from gas mixtures, in particular from hot waste gases with relatively low content of sulphur oxides—such as flue gases and gases originating from roasting processes—has therefore in the past few years become a technical problem.

Although various processes for the purification of gases have been proposed, it is for reasons of heat economy that only a few of these are eligible for the present purpose. Processes aiming at the removal of sulphur oxides at relatively low temperatures are hardly attractive for treating hot waste gases. For these gases which are produced in enormous quantities would then have to be cooled down first and, after removal of the sulphur oxides, heated again in order that they may be removed in a suitable way via a stack. An example of such a low-temperature process is one in which the gas to be purified is washed with a liquid. Another example is a process described in British patent Specification 1,045,045 in which process sulphur compounds are removed by first adsorbing the said compounds at a temperature varying from ambient temperature to about 150°C on a catalyst consisting of vanadium pentoxide and potassium oxide on alumina, and then desorb-

ing and oxidizing the said compounds to sulphur dioxide and sulphur trioxide by means of e.g. air, at a temperature of from 400 to 500°C.

In view of these drawbacks, investigations have been carried out to arrive at a process that is realized at flue-gas temperatures, i.e. at temperatures in the range of about 300—450°C. The purified gases can then be removed via the stack without having to be heated.

A process is known in which the removal or acceptance of sulphur dioxide from hot waste gases is effected at temperatures of about 120—340°C by contacting the said gases with a solid acceptor consisting of an alkali metal oxide supported on alumina or the like as a carrier. A drawback of this known process is that the regeneration of the loaded acceptor—with a reducing gas such as a light aliphatic hydrocarbon—must be effected at a considerably higher temperature of about 600°C.

Surprisingly, it has now been found that the presence of vanadium in an acceptor consisting of an alkali metal compound on a preferably porous carrier material, considerably lowers the temperature required for regeneration of the loaded acceptor. As a consequence a loaded acceptor containing a combination of an alkali metal compound and a vanadium compound can be regenerated with the aid of a reducing gas or gas mixture at the temperatures used for accepting the sulphur oxides from a flue gas or at slightly higher temperatures.

The present invention accordingly provides a process for the removal of sulphur oxides from a gas mixture comprising sulphur oxides and oxygen, in which the said gas mixture is contacted at a temperature above 200°C with a solid acceptor consisting of a solid refractory carrier material comprising a vanadium compound and an alkali metal com-

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pound, said acceptor being capable of taking up sulphur oxides. Particularly, it relates to a process for the removal of sulphur oxides from a hot waste gas, such as a flue gas, the said gas being contacted with the solid acceptor at a temperature of from 300 to 450°C.

5 It should be observed that the term "sulphur oxides" mentioned in this specification refers to both sulphur dioxide and sulphur trioxide. It has been found that under the conditions at which sulphur-dioxide removal is effected with the aid of the acceptor according to the invention any sulphur trioxide present in the feed gas is also accepted.

10 An essential component in the present acceptors is the carrier material. Eligible carriers are, in general, solids which are resistant to high temperatures. As examples of suitable carrier materials may be mentioned natural clays, whether or not pretreated with acid, bauxite, synthetic alumina, silica, silica-alumina and/or silica-magnesia. A very suitable carrier material comprises γ -alumina. For a high degree of loading of the acceptor it is desirable that the carrier material has a relatively large specific surface area; the surface area has preferably to be at least 50 m²/g and more preferably at least 100 m²/g. Surface areas of 150 to 300 m²/g are particularly preferred. Commercial γ -Al₂O₃ grades having an average pore diameter of 65–100 Å, pore volume of 0.30–0.60 ml/g and a specific surface area of 160–230 m²/g are particularly suitable.

35 The acceptor of the invention should contain both an alkali metal compound and a vanadium compound. Preferably, the alkali metal compound is potassium oxide or sodium oxide and the vanadium compound is a vanadium oxide and, more preferably, vanadium pentoxide. An acceptor only containing a vanadium oxide has a very limited capacity for accepting sulphur oxides, whilst an acceptor with only alkali metal oxide has to be regenerated at temperatures of about 600°C or higher.

45 The total metal content of the acceptor may vary within wide limits, again depending on the specific surface area of the carrier material. As a rule it is at least 3%w and preferably 3.5–15%w, calculated on the carrier material. In general the metal content will not exceed 30%w. Preferably the acceptor contains from 2.5 to 15%w of alkali metal and from 1 to 10%w of vanadium, based on the carrier material.

50 The optimum alkali metal content of the acceptor is determined by the nature of the carrier material; when the alkali metal content exceeds a certain limit, part of the alkali metal present apparently does not take part in the reaction with sulphur oxides. As regards the vanadium content, there seems to exist a lower and an upper limit. With an

acceptor having too low a vanadium/alkali metal ratio, the temperature required for the regeneration of the loaded acceptor has to be much higher than the acceptance temperature. Moreover, in that case the sulphur-dioxide content of the regeneration effluent gas, which also comprises hydrogen sulphide, increases to such an extent that difficulties may arise owing to sulphur deposits formed by the reaction of H₂S and SO₂. On the other hand, when the said ratio is rather high, during the acceptance step sulphur oxides will react not only with the alkali metal oxides, but also with other components of the acceptor which may induce disintegration of the acceptor particles. The vanadium and alkali metal of the solid acceptor are therefore preferably present in an atomic ratio vanadium/alkali metal of from 0.1 to 0.8, and more preferably from 0.2 to 0.6.

65 The acceptor used in the process according to the invention may be prepared by known techniques. As an example may be mentioned the method according to which the carrier material is impregnated with an aqueous solution of alkali metal hydroxide or carbonate and a vanadium salt, and subsequently dried and calcined. The impregnating and calcining steps may be repeated as many times as required in order to reach the desired concentrations of vanadium pentoxide and alkali metal oxide. Another possibility is mixing the metal compounds and the carrier material intimately through coprecipitation, with subsequent drying and calcining.

70 As already observed in the foregoing, the present acceptor has a great advantage in that, when loaded with sulphur oxides, it may be regenerated by treatment with a reducing gas or gas mixture at temperatures similar to or slightly higher than those at which the acceptor was loaded. Since the acceptance of sulphur oxides proceeds at temperatures of from 300 to 450°C, regeneration is as a rule effected at temperatures of from 300 to 500°C.

75 Operating at acceptance and regeneration temperatures which differ only slightly is not only of advantage from the point of view of heat economy but is also very important for the lifetime of the acceptor. When, for instance, sulphur dioxide has to be removed from flue gases, an economically justifiable operation of the process will as a rule require that the acceptor serves in the process for a long time. This means that it should be possible to regenerate the acceptor preferably several hundred times without its activity declining too much. A life-time of such a length will not be easy to realize with acceptors that must be heated over a relatively wide temperature range for every regeneration and subsequently be cooled down again for the next acceptance step. The chemical and



physical stability of the acceptors may suffer considerably through such temperature changes.

A suitable reducing gas for the regeneration is, for instance, hydrogen or a gas mixture containing hydrogen and/or carbon monoxide. However, a low-molecular hydrocarbon (that is to say a hydrocarbon which is in the gaseous form at the regeneration temperature and pressure) or a mixture of such hydrocarbons may also be very conveniently applied. As examples may be mentioned low-molecular hydrocarbons such as methane, ethane, propane, butane and the like, or technical mixtures, such as natural gas or tops such as obtained, for instance, in the straight-run distillation of petroleum.

If it is desirable to effect the regeneration of the loaded acceptor at a slightly higher temperature than that at which the acceptance takes place, this higher temperature is easily attained by subjecting part of the reducing gas used to partial combustion in the regeneration reactor.

The acceptance-regeneration cycle described in the foregoing is particularly suitable for a continuous embodiment of the process. Use may be made of the various techniques known for the continuous contacting of a gas with a solid.

In one embodiment of the invention the loaded acceptor is continuously removed from a reactor in which the sulphur oxides are accepted from the gas mixture to be purified, and passed into a second reactor where the loaded acceptor is contacted with a reducing gas, whereupon the acceptor thus treated is recycled to the first reactor. The dimensions of the contact apparatus are so chosen that sufficient loading, or regeneration, of the acceptors is realized and a gas that is substantially free from sulphur oxides is obtained. This continuous purification is by preference conducted in a fluidized acceptor bed, such that the gas to be purified is passed through a vertical reactor either upwards or cross-currently, meanwhile being contacted with acceptor passed through in a downward direction. The purified gases are removed at the top or the side of the reactor, and the loaded acceptor is discharged at the bottom of the reactor and continuously passed into a second reactor, where it is contacted countercurrently with a reducing gas, whereupon the acceptor thus treated is recycled continuously to the first reactor.

In another embodiment of the invention acceptance and regeneration are performed in a gauze tube reactor. According to this embodiment a gas mixture comprising sulphur oxides and oxygen is conducted through a reactor comprising one or more open gas channels running parallel or substantially parallel and having walls designed and built such that the solid acceptor present on, in

and/or behind the said channel walls is freely accessible to the said gas mixture, whilst regeneration of the loaded acceptor is effected in situ by conducting a reducing gas or gas mixture through the said gas channels. An advantage of this technique over a fixed-bed or moving-bed technique is that the presence of solid particles in the gas, such as ash and soot, does not result in clogging and inactivation of the solid acceptor, whilst in addition catalyst attrition and pressure drop are much lower.

The effluent gas from the regeneration of the loaded acceptor, which is considerably richer in sulphur compounds than the original oxygen-containing gas mixture, may be worked up in a known manner, either to elementary sulphur or to sulphuric acid.

As stated hereinbefore, the said effluent gas may also comprise sulphur dioxide. In order to avoid solid sulphur deposits being formed, it may be desirable to conduct the regeneration effluent gas through a medium which catalyses the reaction of the said oxide and the reducing gas used to give hydrogen sulphide. According to British patent Specification 1,116,129, vanadium pentoxide is a suitable catalyst for this purpose.

The invention is further elucidated by means of the following examples describing acceptors consisting of potassium oxide and vanadium pentoxide on γ -alumina as the carrier.

EXAMPLE I

In order to study the influence of the vanadium-potassium atomic ratio of the acceptor on its capacity for accepting sulphur dioxide from waste gases, a number of acceptors having varying V/P ratios were prepared. All acceptors contained a fixed amount of potassium, viz. 5%w on carrier material, and had different amounts of vanadium, varying from 1 to 10%w. The acceptors were prepared as follows:

A commercial γ -alumina with grain sizes varying between 0.5 and 1.9 mm (35—10 mesh, U.S. Sieve Series), an average pore diameter of 67 Å, a pore volume of 0.34 ml/g and a specific surface area of 162 m²/g, was impregnated at room temperature with an aqueous solution of potassium hydroxide and vanadyl oxalate, subsequently dried at 120°C and then calcined at 500°C for three hours.

The acceptors thus prepared were tested for their capacity for the removal of SO₂ from a synthetic flue gas of the following composition: CO₂ 13.5%v; O₂ 6.1%v; N₂ 74.5%v; H₂O 5.5%v; SO₂ 0.3%v. The acceptor to be tested was placed in a tubular reactor and the above gas mixture was passed over it at a temperature of 300°C for 3 hours with a space velocity of 2000 litres of gas per litre of acceptor per hour. The sulphur dioxide load of the acceptor at the moment of breakthrough of 10% of the sul-

phur dioxide in the gas feed was noted. Thereafter the loaded acceptor was regenerated for 5 hours with methane as a reducing gas, at a temperature of 450°C and a space velocity of 100 litres/litres.h. After regener-

ation the acceptor was treated again with the synthetic flue gas. The results obtained are shown in Table I in which the figures for sulphur-dioxide load are average values obtained in 10 acceptance-regeneration cycles.

TABLE I

K, %w on γ -Al ₂ O ₃	V, %w on γ -Al ₂ O ₃	V/K atomic ratio	SO ₂ load, %w on acceptor
5	1.5	0.2	2.0
5	2.8	0.4	3.5
5	4.0	0.6	4.1
5	10.0	1.5	6.0

It should be observed that when all potassium oxide present has been converted into potassium sulphate, the sulphur dioxide load of the acceptors amounts to about 4%w for the above example. This implies that at a vanadium content of more than 4%w sulphur oxides are apparently bound by other components of the acceptor as well.

prepared by impregnating 60 grams of γ -Al₂O₃ of Example I at room temperature with 60 ml of a liquid comprising 4.48 grams of KOH, 2.99 grams of V₂O₅ and 6 grams of oxalic acid. The impregnated alumina was left for 15 minutes and then dried at 120°C and calcined for 3 hours at a temperature of 500°C.

EXAMPLE II

To assess the lifetime of the acceptors of the invention an acceptor containing 5.2%w of potassium and 2.8%w of vanadium on γ -alumina was tested in a series of 32 acceptance-regeneration cycles. The acceptor was

20 ml of this acceptor was tested under the same conditions as described in Example I. Regeneration of the loaded acceptor was, however, done at 400°C with propane instead of methane (space velocity of 100 litres per litre of acceptor per hour).

TABLE II

Cycle number	2—4	5—12	13—15	16—32
SO ₂ —load at the moment of breakthrough of 10% of SO ₂ in feed gas, %w on acceptor	4.1	—	3.4—4.0	3.0
Regeneration in hours	5	5	16	5

From the results given it is evident that after 32 cycles hardly any decline of the performance of the acceptor occurs. During regeneration no coke deposited on the acceptor.

acceptor with 10.4%w of potassium (V/K atomic ratio 0.2) amounts to 4.0%w, as compared with 3.5%w for the acceptor containing 5.2%w of potassium (V/K atomic ratio 0.4).

EXAMPLE III

Test results with an acceptor prepared as described in Example II but having twice the quantity of potassium (10.4%w on alumina) showed that an increase of the potassium content of the acceptor has only little effect on acceptance properties. At the moment of breakthrough of 10% of SO₂ in the feed gas, the sulphur-dioxide load of the

EXAMPLE IV

In order to study the influence of the properties of the alumina carrier, experiments were performed with two acceptors on carriers having different properties, both acceptors comprising 5.2%w of potassium and 2.8%w of vanadium, based on alumina. Acceptor A contained γ -alumina as described in Example

I, whilst the γ -alumina used for acceptor B had the following properties: average pore diameter 100 Å, pore volume 0.56 ml/g, specific surface area 229 m²/g. Conditions

during acceptance and regeneration were equal to those mentioned in Example I. The results are shown in Table III.

TABLE III

Acceptor	Period from start to breakthrough of 10% of SO ₂ in the feed, min.				SO ₂ -load at the moment of breakthrough of 10% of SO ₂ in the feed, %w on acceptor			
	A		B		A		B	
Particle size of acceptor, mm.	0.5—1.4	3	0.5—1.4	3	0.5—1.4	3	0.5—1.4	3
Cycle No.								
2	>195	50	85	60	>4.2	0.9	3.0	2.2
3	>195	40	85	60	>4.1	0.8	3.0	2.2
4	195	25	85	85	4.1	0.5	3.0	3.0

EXAMPLE V

For comparison acceptors containing exclusively potassium or vanadium were also tested according to the procedure of Example I.

An acceptor containing 10%w of potassium on γ -alumina showed an excellent performance during acceptance, but regeneration could only be effected at very high temperatures, viz. in the range of from 600 to 700°C.

The performance of an acceptor containing 2.8%w of vanadium on the same carrier material was very poor; already at the very outset of an experiment conducted at 400°C, 60 to 80% of the sulphur dioxide intake appeared in the off-gas.

In all experiments described hereinbefore the sulphur oxides were removed from the flue gases at a temperature of 300°C. Similar experiments at higher temperatures, e.g. at 450°C, showed no significant differences except for a higher rate of acceptance, as could be expected.

In our British patent application (Serial No. 1,154,008) 53,141/66, a process and apparatus as described and claimed for the removal of sulphur oxides from a gaseous mixture comprising sulphur oxides and oxygen by means of a solid acceptor suitable for accepting sulphur oxides. In the process, the gaseous mixture comprising sulphur oxides and oxygen is conducted through one or more open gas channels running parallel or substantially parallel and having walls designed and built such that acceptor material present on, in and/or behind said channel walls is freely accessible to said gas mixture.

WHAT WE CLAIM IS:—

1. A process for the removal of sulphur oxides from a gas mixture comprising sulphur oxides and free oxygen, in which the said gas mixture is contacted at a temperature above 200°C with a solid acceptor consisting of a solid refractory carrier material comprising a vanadium compound and an alkali metal compound, said acceptor being capable of taking up sulphur oxides.

2. A process as claimed in claim 1, in which the gas mixture comprising sulphur oxides and oxygen is a hot waste gas, such as a flue gas.

3. A process as claimed in claim 1 or 2, in which the gas mixture as defined is contacted with the solid acceptor at a temperature of from 300° to 450°C.

4. A process as claimed in any one of claims 1 to 3, in which the solid carrier material is alumina, silica, silica-alumina and/or silica-magnesia.

5. A process as claimed in claim 4, in which the solid carrier material is γ -alumina.

6. A process as claimed in any one of claims 1 to 5, in which the carrier material has a specific surface area of at least 50 m²/g.

7. A process as claimed in any one of claims 1 to 6, in which the alkali metal compound is potassium oxide.

8. A process as claimed in any one of claims 1 to 7, in which the vanadium compound is a vanadium oxide, preferably vanadium pentoxide.

9. A process as claimed in any one of claims 1 to 8, in which the solid acceptor comprises from 2.5 to 15%w of alkali metal



I, whilst the γ -alumina used for acceptor B had the following properties: average pore diameter 100 Å, pore volume 0.56 ml/g, specific surface area 229 m²/g. Conditions

during acceptance and regeneration were equal to those mentioned in Example I. The results are shown in Table III.

TABLE III

Acceptor	Period from start to breakthrough of 10% of SO ₂ in the feed, min.				SO ₂ -load at the moment of breakthrough of 10% of SO ₂ in the feed, %w on acceptor			
	A		B		A		B	
Particle size of acceptor, mm.	0.5—1.4	3	0.5—1.4	3	0.5—1.4	3	0.5—1.4	3
Cycle No.								
2	>195	50	85	60	>4.2	0.9	3.0	2.2
3	>195	40	85	60	>4.1	0.8	3.0	2.2
4	195	25	85	85	4.1	0.5	3.0	3.0

EXAMPLE V

For comparison acceptors containing exclusively potassium or vanadium were also tested according to the procedure of Example I.

An acceptor containing 10%w of potassium on γ -alumina showed an excellent performance during acceptance, but regeneration could only be effected at very high temperatures, viz. in the range of from 600 to 700°C.

The performance of an acceptor containing 2.8%w of vanadium on the same carrier material was very poor; already at the very outset of an experiment conducted at 400°C, 60 to 80% of the sulphur dioxide intake appeared in the off-gas.

In all experiments described hereinbefore the sulphur oxides were removed from the flue gases at a temperature of 300°C. Similar experiments at higher temperatures, e.g. at 450°C, showed no significant differences except for a higher rate of acceptance, as could be expected.

In our British patent application (Serial No. 1,154,008) 53,141/66, a process and apparatus as described and claimed for the removal of sulphur oxides from a gaseous mixture comprising sulphur oxides and oxygen by means of a solid acceptor suitable for accepting sulphur oxides. In the process, the gaseous mixture comprising sulphur oxides and oxygen is conducted through one or more open gas channels running parallel or substantially parallel and having walls designed and built such that acceptor material present on, in and/or behind said channel walls is freely accessible to said gas mixture.

WHAT WE CLAIM IS:—

1. A process for the removal of sulphur oxides from a gas mixture comprising sulphur oxides and free oxygen, in which the said gas mixture is contacted at a temperature above 200°C with a solid acceptor consisting of a solid refractory carrier material comprising a vanadium compound and an alkali metal compound, said acceptor being capable of taking up sulphur oxides.

2. A process as claimed in claim 1, in which the gas mixture comprising sulphur oxides and oxygen is a hot waste gas, such as a flue gas.

3. A process as claimed in claim 1 or 2, in which the gas mixture as defined is contacted with the solid acceptor at a temperature of from 300° to 450°C.

4. A process as claimed in any one of claims 1 to 3, in which the solid carrier material is alumina, silica, silica-alumina and/or silica-magnesia.

5. A process as claimed in claim 4, in which the solid carrier material is γ -alumina.

6. A process as claimed in any one of claims 1 to 5, in which the carrier material has a specific surface area of at least 50 m²/g.

7. A process as claimed in any one of claims 1 to 6, in which the alkali metal compound is potassium oxide.

8. A process as claimed in any one of claims 1 to 7, in which the vanadium compound is a vanadium oxide, preferably vanadium pentoxide.

9. A process as claimed in any one of claims 1 to 8, in which the solid acceptor comprises from 2.5 to 15%w of alkali metal

and from 1 to 10%w of vanadium, based on the carrier material.

- 5 10. A process as claimed in any one of claims 1 to 9, in which the vanadium and alkali metal of the solid acceptor are present in an atomic ratio vanadium/alkali metal within the range of from 0.1 to 0.8, preferably from 0.2 to 0.6.

- 10 11. A process as claimed in any one of claims 1 to 10, in which after acceptance the sulphur oxide-loaded acceptor is regenerated by treatment with a reducing gas or gas mixture.

- 15 12. A process as claimed in claim 11, in which the loaded acceptor is regenerated at temperatures similar to or slightly higher than those at which the solid acceptor was loaded.

- 20 13. A process as claimed in claim 11 or 12, in which the loaded acceptor is regenerated at a temperature in the range of from 300 to 500°C.

- 25 14. A process as claimed in any one of claims 11 to 13, in which the reducing gas or gas mixture is hydrogen, and/or carbon monoxide, and/or a low-molecular hydrocarbon or mixture of such hydrocarbons.

- 30 15. A process as claimed in claim 14, in which the low-molecular hydrocarbon is methane, ethane, propane, butane or mixtures thereof.

- 35 16. A process according to any one of the preceding claims, in which the loaded acceptor is continuously removed from a reactor in which the sulphur oxides are accepted from the gas mixture to be purified, and passed

into a second reactor where the loaded acceptor is contacted with a reducing gas, whereupon the acceptor thus treated is recycled to the said first reactor.

- 40 17. A process according to any one of the claims 1 to 15, in which the gas mixture comprising sulphur oxides and oxygen is conducted through a reactor comprising one or more open gas channels running parallel or substantially parallel and having walls designed and built such that the solid acceptor present on, in and/or behind the said channel walls is freely accessible to the said gas mixture, whilst regeneration of the loaded acceptor is effected in situ by conducting a reducing gas or gas mixture through the said gas channels.

- 50 18. A process as claimed in any one of the preceding claims, substantially as hereinbefore described with special reference to any of the Examples I to IV.

- 55 19. A gas which has been subjected to a process according to any one of the preceding claims.

- 60 20. A gas comprising hydrogen sulphide and/or sulphur oxides and obtained by regeneration of the solid acceptor employed in a process according to any one of claims 1—18.

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