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**DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION**(1) Here
insert (in
full) Name of
Company.In support of the Convention Application made by⁽¹⁾.....
HALDOR TOPSOE A/S(2) Here
insert title
of Invention.(hereinafter referred to as the applicant) for a Patent
for an invention entitled:⁽²⁾.....
PURIFICATION OF SULPHIDE-CONTAINING GASES(3) Here
insert full Name
and Address,
of Company
official
authorized
to make
declaration.We ⁽³⁾..... J. ROSTRUP-NIELSEN and POUL THYGESEN, both
of..... Nymollevvej 55, DK-2800 Lyngby, Denmark

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent
to make this declaration on its behalf.(4) Here
insert basic
Country or
Countries
followed by
date or dates
and basic
Applicant or
Applicants.2. The basic application as defined by Section 141 of the Act was
made in⁽⁴⁾..... Denmark
on the 29th day of May 1989, by
HALDOR TOPSOE A/S~~on the~~ ~~day of~~ ~~19~~ ~~by~~(5) Here
insert (in
full) Name
and Address
of Actual
Inventor or
Inventors.3.⁽⁵⁾ POUL ERIK HOJLUND NIELSEN, Rolandsvej 3, DK-3480
Fredensborg, Denmarkis/~~are~~ the actual inventor of the invention and the facts upon which the applicant
is entitled to make the application are as follow:The applicant is the assignee of..... the invention from the said
actual inventor4. The basic application referred to in paragraph 2 of this Declaration
was..... the first application made in a Convention country in
respect of the invention the subject of the application.DECLARED at Lyngby Denmark
this..... Tues day of 23rd October 1990

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PURIFICATION OF SULPHIDE-CONTAINING GASES

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(56) Prior Art Documents
EP 71983
WO 86/02576
DE 2759049

(57) Claim

1. A process for the removal of sulphides from a gas stream by contacting the sulphide-containing gas stream with a solid absorbent containing tin, tin oxides or mixtures thereof and optionally a stabilizing component; sulphidizing the solid absorbent and desulphidizing the gas stream; and regenerating the sulphidized absorbent, characterized in regenerating the absorbent exclusively by contacting it with a stream of steam.

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		628994	

(54) Title: PURIFICATION OF SULPHIDE-CONTAINING GASES

(57) Abstract

The removal of sulphides from gas streams while using a solid absorbent containing tin, tin oxides or mixtures thereof and optionally a stabilizing component consisting of nickel, copper, cobalt, iron or oxides thereof takes place by contacting the sulphide-containing gas stream with the solid absorbent, which is expediently in the form of a carrier with the tin component and the stabilizing component; hereby the absorbent is sulphided and the gas stream desulphided. Subsequently the sulphided absorbents are regenerated by being contacted with a stream of steam. The regeneration process employed is substantially thermoneutral so that superheating and consequent sintering of the absorbent is avoided; moreover it is not necessary to operate at low temperatures, whereby the formation of sulphates as a by-product is avoided.

PURIFICATION OF SULPHIDE-CONTAINING GASES

Field of the Invention

The present invention relates to a process for gas
5 purification, and more particularly to a regenerative
process for removal of gaseous sulphides in hot gas
streams. The invention further relates to a solid absorbent
for use in such process.

Industrial gases, such as feed gases for chemical
10 synthesis or off-gases from plant operation, often contain
high levels of sulphur compounds which were part of the feed
stock. Removal of sulphur compounds from sulphur-containing
gases is necessary to meet environmental quality standards
or to avoid damage of equipment.

15

Background of the Invention

Conventionally used solid absorbents in desulphur-
ization processes are activated carbon, iron oxide and zinc
oxide.

20 A solid acceptor comprising supported platinum group
metals in association with copper, germanium, rhenium or tin
compounds is mentioned in GB Patent No. 1,592,378. The
acceptor as described is used in the separation of sulphur
dioxide from a gaseous mixture containing sulphur dioxide
25 and oxygen.

Sulphur in sulphur-containing fuel, however, is
available in many processes as gaseous sulphides such as
hydrogen sulphide, carbonyl sulphide and carbon disulphide
or related compounds, such as mercaptans.

30 Removal of gaseous sulphide-compounds is usually
achieved by cold scrubbing processes with liquid absorbents,
such as alkanolamines.

The known scrubbing methods disadvantageously require
cooling of treated gases, resulting in thermally less
35 efficient processes.

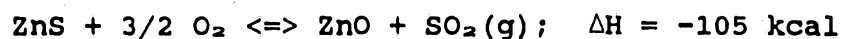
Certain drawbacks of the known scrubbing processes
can be avoided by the use of solid gas purification systems

including the use of solid sulphide absorbents like metal oxides, which operate at higher temperatures.

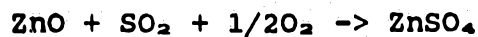
A process for removing hydrogen sulphide from gases is mentioned in EP Application No. 159,05. By this process a hydrogen sulphide containing gas is contacted at a temperature above 300°C with a solid absorbent comprising a mixture of zinc oxide and a zeolite. Spent absorbent is regenerated by passing an oxygen-containing gas over the absorbent at a temperature above 400°C.

Several other absorbents based on zinc oxide are described in the literature. Thus, zinc ferrite was recently proposed as absorbent of this type. Zinc ferrite ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$) is a regenerative absorbent which works at high temperatures. During the gas desulphurization step the zinc and iron oxides are converted into the corresponding sulphides, which can be regenerated to the oxides by using oxidizing gases such as oxygen or air at elevated temperatures.

According to the following reactions:



the regeneration of ZnS is a highly exothermic reaction resulting in sintering of the absorption mass at elevated temperatures and in decreased desulphurization capacity of the absorbent caused by structural changes. To minimize sintering a proper control of the reaction temperature and atmosphere is necessary to stabilize the temperature within narrow ranges during the regeneration step. Lower temperatures, however, lead to a significant degree of zinc sulphate formation via the following reactions:



This is deleterious to the overall process in that the presence of sulphates not only reduces the sulphur capacity of the sorbent but also leads to the introduction of SO_2 into the hot gas stream.

5 It is therefore an object of the present invention to provide a process for the purification of sulphide-containing gases without the disadvantages of the known processes.

According to the invention, there is provided a
10 regenerative process for the removal of sulphides from a gas stream by using a solid absorbent comprising tin, tin oxides or mixtures thereof and optionally a stabilizing component, which process comprises the steps of contacting a sulphide-
15 the solid absorbent and desulphidizing the gas stream; and regenerating the sulphidized absorbent by contacting the sulphidized absorbent with a stream of steam.

In a preferred embodiment of the regenerative process according to the invention, the sulphide containing gas
20 stream is contacted at a temperature of between 200°C and 600°C with the absorbent.

In a particularly preferred embodiment of the regenerative process according to the invention, the sulphidized absorbent is contacted at a temperature of
25 between 300°C and 500°C with the stream of steam.

A further object of the present invention is to provide a regenerative absorbent for use in the process as described above, which absorbent comprises as absorption component at least one component selected from the group
30 consisting of metallic tin, tin oxides and mixtures thereof.

In a preferred embodiment of the solid absorbent according to the invention the active absorption component is supported on a carrier material.

The carrier material for use in the inventive
35 absorbent may be any known refractory materials which are stable at elevated temperatures. Suitable carrier materials are clays, silicates, alumina and titania.

Preferably, the carrier material is alumina or titania.

As tin is the active sulphide-capturing material the absorbent contains preferably at least 5% by weight of tin, 5 tin oxides, or mixtures thereof.

In addition to the absorption component the solid absorbent according to the invention may further comprise a stabilizing component selected from group consisting of the oxides of copper, nickel, cobalt and iron.

10 The inclusion of the second component stabilizes the absorbent by forming an alloy with tin and thereby increasing the melting point of tin, which is formed during the purification of highly reducing gas mixtures.

A very dramatic raise of the melting point is seen in 15 tin-iron alloys containing from 0.01 atom% to 20 atom% iron.

Accordingly, a particular preferred embodiment of the solid absorbent according to the invention comprises tin oxide as the active absorption component and from 0.01 atom% to 20 atom% of the active absorption-component iron.

20 According to the invention, the solid absorbent as mentioned hereinbefore may be prepared by any convenient method.

The absorbent is advantageously prepared by impregnating the carrier with an impregnation solution 25 comprising the desired metal compounds and transforming the absorbent in a subsequent calcination step to its active form. Suitable tin salts for use in the impregnation solution are tin hydroxide and tin halogenides.

For the preparation of stabilized absorbents 30 according to a preferred embodiment of the invention the impregnation solution further comprises salts of copper, nickel, cobalt or iron. Useful copper, nickel, cobalt and iron salts are any salts which by heating in a reducing atmosphere can be converted to their metallic form.

35 In a particularly preferred method the absorbent is prepared by pulverizing and intimately mixing particles of desired metal compounds and carrier material, succeeded by

calcination to bring the absorbent in its active form for absorption of gaseous sulphides.

The activated absorbent may be used in any convenient shape, such as extrudates, tablets, pellets, granules, pills or powder.

In accordance with the inventive process the solid absorbent may be used in fixed bed manner in one or more reactors which operate alternately between absorption and regeneration phases. It may also be used in a fluidized bed and regenerated in a separate reactor.

During the absorption phase, sulphide-containing gases are passed through the reactor at a temperature between 200°C and 600°C, as usually provided by the hot gases to be purified. Gaseous sulphides are thereby absorbed by tin and tin oxide according to one or more of the following reactions:

- (1) $\text{Sn} + \text{H}_2\text{S} \rightleftharpoons \text{SnS} + \text{H}_2 \quad \Delta H_o = -19 \text{ kcal/mole}$
- (2) $\text{SnO}_2 + \text{H}_2 + \text{H}_2\text{S} \rightleftharpoons \text{SnS} + 2\text{H}_2\text{O}; \Delta H_o = 4 \text{ kcal/mole}$
- (3) $\text{SnO}_2 + \text{H}_2 + \text{RSH} \rightleftharpoons \text{SnS} + \text{H}_2\text{O} + \text{ROH}$
- (4) $\text{SnO}_2 + \text{H}_2 + \text{COS} \rightleftharpoons \text{SnS} + \text{CO}_2 + \text{H}_2\text{O} \quad \Delta H_o = 4 \text{ kcal/mole}$

Regeneration of spent absorbent is predominantly effected by the reversed and substantially thermoneutral reaction (2) by passing a stream of hot steam through the reactor during the regeneration phase.

Since the regeneration thereby proceeds by nearly thermoneutral reactions the temperature during the regeneration phase may vary within wide ranges.

The regeneration phase is advantageously carried out at temperatures between 300°C and 500°C though lower temperatures are permissible without any risk of sulphate formation.

Further advantages and objects of the invention will become obvious from the following not-limiting examples, which more fully illustrate the improvement in gaspurification as obtained by the preferred embodiments of the

invention.

Example 1

5 This example describes the preparation of a solid absorbent according to the invention comprising tin dioxide impregnated on alumina.

 240 g of conventional alumina is suspended as 3 mm extrudates in an impregnation solution containing 40 g tin
10 dichloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 120 ml demineralized water.

 The extrudates are allowed to stand in the impregnation solution at 20°C for 15 minutes, after which the impregnated extrudates are filtered and dried at 110°C
15 for 16 hours.

 The absorbent so formed is transformed to its active form containing 7.6 wt% tin by immersion in 200 ml of demineralized water having dissolved therein 40 g of sodium hydroxide at 20°C for 15 minutes and subsequently
20 calcination at 500°C for one hour by which tin monoxide obtained by the reaction with sodium hydroxide is oxidized to tin dioxide.

Example 2

25 -----

 In this example a method for the preparation of a solid absorbent according to the invention is described.

 130 g of the alumina described in Example 1 is suspended in 600 ml demineralized water and turbomixed at
30 20°C. After 30 minutes, 60 g of SnO_2 are added to the slurry. The turbomixing is continued for another 30 minutes, after which the slurry is dried at 110°C for 16 hours.

 The dried product, containing 14.9 wt% Sn, is mechanically ground and formed to tablets with a diameter of
35 4.5 mm and a height of 4.0 mm.

 The tablets are finally calcinated at a temperature of about 400°C for 1 hour.

Example 3

The absorption capacity and regenerability of the absorbent as prepared in example 1 is evaluated in 3

5 subsequent absorption and regeneration cycles.

80 g of the absorbent is charged as a 400 mm high fixed bed in a tubular reactor with 18 mm inside diameter, provided with a 3 mm thermostate case. Feed gas comprising

10 66 vol% H₂
 32 vol% CO
 1 vol% CO₂
 0.5 vol% CH₄ and
15 600-800 vol ppm H₂S

is generated by cracking methanol and ammonium sulphide. The content of hydrogen sulphide in the feed gas is continuously analyzed by means of a Dräger^(R) tube at the inlet and outlet side of the reactor.

20 The gas flow into and out of the reactor is measured by means of a conventional dry gas metering apparatus.

During the absorption phases feed gas comprising about 15 vol% water vapour is passed through the reactor at a space velocity between 250 and 420 Nl/h and a temperature
25 between 365 and 472°C as specified below.

The breakthrough time is determined graphically when the content of H₂S in the outlet gas of the reactor increases abruptly in a given time interval between two H₂S-analyses.

Regeneration of spent absorbent is commenced after 17
30 hours, 300 minutes and 270 minutes of the first, second the third absorption phase, respectively.

At the regeneration phase steam is passed through the reactor at a space velocity of 521 Nl/h and a temperature between 370 and 450°C for 525 minutes, 480 minutes and 350
35 minutes of the first, second and third regeneration, respectively.

During the regeneration the content of desorbed H_2S in the outlet gas from the reactor is continuously measured by means of a Dräger^(R) tube. The process parameters and the results of the absorption and regeneration tests are

5 tabulated below in Table 1.

Table 1

	Temp., °C	Pressure, bar	Flow inlet, Nl/h	H ₂ S, inlet/outlet, before break-through ppm	Absorption efficiency, % H ₂ S absorbed	Break-through time, min.	Load at break-through, mol H ₂ S per mol SnO ₂	Regeneration efficiency, mol desorbed H ₂ S per mol absorbed H ₂ S
1st absorption	368-415	25	252	800/30	96.3	210	0.73	
1st regeneration	367-404	10	521					0.97
2nd absorption	365-412	25	419	650/17	97.4	180	0.74	
2nd regeneration	376-404	10	521					0.84
3rd absorption	408-472	25	420	660/90	85.0	180	0.73	
3rd regeneration	388-443	10	521					0.92

The data of table 1 clearly show that the absorption efficiency of this absorbent is nearly constant within a wide range of operation conditions.

5 Example 4

A preferred embodiment of the invention is related to a stabilized solid absorbent comprising tin dioxide and nickel oxide.

10 130 g of alumina extrudates, as described in Example 1, are suspended in 600 ml demin. water and turbomixed at 20°C for 15 minutes. 60 g of SnO_2 are added and turbomixing is continued at 20°C for another 15 minutes after which 12.3 g of basic nickel carbonate ($\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) are added.

15 The slurry is maintained at 20°C and turbomixed for additional 30 minutes.

The mixture formed is dried at 110°C for 126 hours.

The dried product containing 24.0 wt% Sn and 2.9 wt% Ni is mechanically ground and formed to tablets with a
20 diameter of 4.5 mm and a height of 4.0 mm.

The tablets are finally calcined at a temperature of about 400°C for 1 hour, which leaves the absorbent in its active form.

25 Examples 5-6

In the preparation of a solid absorbent representative of other stabilized absorbents according to the invention basic nickel carbonate is replaced by basic copper
30 carbonate ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) or basic cobalt carbonate ($2\text{CoCO}_3 \cdot \text{Co}(\text{OH})_2 \cdot \text{H}_2\text{O}$), and the preparation is carried out in substantially the same manner as described in Example 4.

Example 7

35 -----

In this Example the preparation of a particularly preferred stabilized absorbent comprising iron as stabil-

izing component is described.

130 g of alumina extrudates, as described in Example 1, are suspended in 600 ml demin. water and turbomixed at 20°C for 15 min. 60 g of SnO_2 are added and turbomixing is continued at 20°C for another 15 min. after which 8.2 g of Fe_2O_3 are added.

The slurry is maintained at 20°C and turbomixed for additional 30 min.

The mixture formed is dried at 110°C for 16 hours.

The dried product containing 23.8 wt% Sn and 2.9 wt% Fe is mechanically ground and formed to tablets with a diameter of 4.5 mm and a height of 4.0 mm.

The tablets are finally calcined at a temperature of about 400°C for 1 hour.

Example 8

The absorption capacity and regenerability of the copper stabilized absorbent prepared in Example 5 is evaluated by 6 subsequent absorption and regeneration cycles by the procedure described in Example 3.

92.7 g of the absorbent comprising 0.19 mol% Sn and 0.04 mol% Cu, calculated on the total amount of the absorbent, are charged in the reactor.

The flow of feed gas comprising about 15 vol% water vapour through the reactor at the absorption phase is measured continuously and varies between 340 and 505 Nl/h at a temperature between 400 and 510°C.

During the absorption phases the content of H_2 and H_2S in the feed gas varies as summarized in Table 2 below.

Table 2

		Absorption No.					
		1	2	3	4	5	6
5							
	vol% H ₂	66	66	72	72	72	72
	vol% CO	32	32	14	14	14	12
	vol% CO ₂	1	1	13	13	13	15
	vol% CH ₄	0.5	0.5	0.2	0.2	0.2	0.6
10	vol ppm H ₂ S	750	3600	4000	3700	4900	8800

During the regeneration phase steam is passed through the reactor at a space velocity of about 250-530 Nl/h and a temperature of 350-560°C as further specified in Table 3.

Table 3

	Time min.	Temp., °C	Pres- sure, bar	Flow inlet Nl/h	H ₂ S, inlet/ outlet, be- fore break- through ppm	Absorp- tion ef- ficiency, % H ₂ S absorbed	Break- through, time, min.	Load at break- through, mol H ₂ S per mol SnO ₂	Regenera- tion effi- ciency, mol absorbed H ₂ S per mol desorbed H ₂ S	Corrected for H ₂ S dissolved in H ₂ O
1st absorption	1370	364-412	25	340	750/26	96.5	940	0.72		
1st regeneration	745	342-391	10	521					0.83	1.0
2nd absorption	1150	357-405	25	355-403	3600/65	98.2	945	1.32		
2nd regeneration	1575	349-393	10	524					*	
3rd absorption	310	363-401	25	406	4000/200	95.0	90	1.95		
3rd regeneration	1410	352-394	10	526					*	
4th absorption	440	407-457	25	405	3700/190	94.8	100	0.95		
4th regeneration	450	391-446	10	523					0.83	1.0
5th absorption	195	407-457	25	409	4900/230	95.3	100	1.05	0.75	1.0
5th regeneration	425	392-447	10	521						
6th absorption	245	423-459	25	195	8800/230	97.4	120			
6th regeneration	450	409-450	10	256					0.88	1.0

* missing values

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the removal of sulphides from a gas stream by contacting the sulphide-containing gas stream with a solid absorbent containing tin, tin oxides or mixtures thereof and optionally a stabilizing component; sulphidizing the solid absorbent and desulphidizing the gas stream; and regenerating the sulphidized absorbent, characterized in regenerating the absorbent exclusively by contacting it with a stream of steam.
2. The process as claimed in claim 1, characterized in contacting the sulphidized absorbent at a temperature of between 300°C and 500°C with the stream of steam.

DATED this 23rd day of July 1992.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 90/00115

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: B 01 D 53/34, C 10 K 1/20		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	B 01 D; B 01 J; C 10 K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
SE,DK,FI,NO classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP, A2, 0071983 (VEG-GASINSTITUUT N.V.) 16 February 1983, see page 9, line 24 - page 10, line 16; page 12, line 16 - line 25; page 14, line 19 - line 27; page 39, line 21 - line 23 --	1-2,4- 10
Y	WO, A1, 8602576 (HENNING, K-D) 9 May 1986, see page 3, line 6 - line 16; page 5, line 3 - line 8; page 6, line 19 - line 26; claims 1-6 --	1-2,3-6, 9,10
Y	DE, A1, 2759049 (HITACHI, LTD.) 6 July 1978, see page 7, line 8 - line 29 -- -----	1,3
¹⁰ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
21st August 1990		1990 -08- 23
International Searching Authority		Signature of Authorized Officer
SWEDISH PATENT OFFICE		Britt-Marie Lundell

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/DK 90/00115**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on **90-08-02**
The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A2- 0071983	83-02-16	AU-B-	559024	87-02-19
		AU-D-	8695982	83-02-10
		CA-A-	1196477	85-11-12
		DE-A-C-	3131257	83-02-24
		JP-A-	58036620	83-03-03
		US-A-	4478800	84-10-23

WO-A1- 8602576	86-05-09	DE-A-	3438770	86-04-24
		JP-T-	62500575	87-03-12

DE-A1- 2759049	78-07-06	JP-A-	53085805	78-07-28
		US-A-	4155990	79-05-22
		JP-A-	53104605	78-09-12
		JP-A-	53104606	78-09-12