

AUSTRALIA

Patents Act 1990

658472

PATENT REQUEST : STANDARD PATENT

I/We, being the person/s identified below as the Applicant, request the grant of a patent to the person/s indicated below as the Nominated Person/s, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71] [70] Applicant/s and Nominated Person/s:
Kronos Titan GmbH,
of Peschstrasse 5, D-5090 Leverkusen 1, GERMANY

[54] Invention Title:
Catalyst for carbonsulfide hydrolysis

[72] Name/s of actual inventor/s: (optional)

[74] Address for service in Australia:
DAVIES COLLISON CAVE, Patent Attorneys
10 Barrack Street, SYDNEY NSW 2000

Attorney Code : CA

BASIC CONVENTION APPLICATION/S DETAILS:

[31] Appln No.:
P 42 06 913.0

[33] Country:
GERMANY

Code:
DE

[32] Date:
5 March 1992

DATED this TENTH day of FEBRUARY 1993

Kronos Titan GmbH
By Patent Attorneys
DAVIES COLLISON CAVE

Peter Stearne

Dr. PETER STEARNE, FIPAA

Fee: \$ 189.00

S 035355

100293

A U S T R A L I A

Patents Act 1990

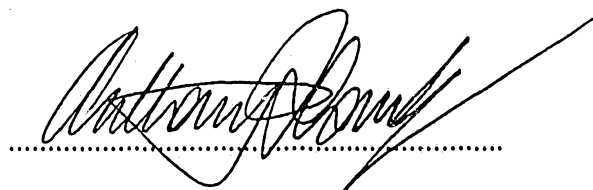
NOTICE OF ENTITLEMENT

KRONOS TITAN GMBH, of Peschstrasse 5, D-5090 Leverkusen 1, Germany being the applicant/Nominated Person in respect of the Application No. 32980/93 state the following:

The Nominated Person is entitled to the grant of the patent because the Nominated Person derives title to the invention from the inventors, ACHIM HARTMANN by assignment.

The Nominated Person is entitled to claim priority from the basic application listed on the patent request form because the Nominated Person made the basic application listed on the patent request form, and because the basic application is the first application made in a Convention country in respect of the invention.

Dated this 4th day of January, 1995



a member of the firm of
DAVIES COLLISON CAVE
for and on behalf of
the applicant(s).



AU9332980

(12) PATENT ABRIDGMENT (11) Document No. AU-B-32980/93
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 658472

- (54) Title
HYDROLYSIS OF CARBONYL SULPHIDE AT ELEVATED TEMPERATURE WITH TIO₂ CATALYST
- International Patent Classification(s)
(51)⁵ C01B 003/26 B01D 053/36
- (21) Application No. : 32980/93 (22) Application Date : 10.02.93
- (30) Priority Data
- (31) Number (32) Date (33) Country
4206913 05.03.92 DE GERMANY
- (43) Publication Date : 09.09.93
- (44) Publication Date of Accepted Application : 13.04.95
- (71) Applicant(s)
KRONOS TITAN GMBH
- (72) Inventor(s)
ACHIM HARTMANN
- (74) Attorney or Agent
DAVIES COLLISON CAVE , GPO Box 3876, SYDNEY NSW 2001
- (56) Prior Art Documents
BE 895359
EP 60741
- (57) Claim

1. A process for the hydrolysis of carbonyl sulfide in a gas mixture which is passed through a titanium dioxide catalyst at an increased temperature, wherein sintered titanium dioxide particles are used as the catalyst.

2. The process according to claim 1, wherein titanium dioxide particles are used which are obtained as a by-product in the large-scale technical production of titanium dioxide using the chloride process and which are used as scrub-solids for maintaining the heat transfer during indirect cooling of the reaction gases of the gaseous phase oxidation of titanium tetrachloride.

3. The process according to claim 1 or 2, wherein titanium dioxide particles which have been treated prior to use with a sodium hydroxide solution or a sodium aluminate solution are used for the catalyst.

4. The process according to claim 1, 2 or 3, wherein the temperature of the catalyst is above 60°C.

6. The process according to any one of claims 1 to 5, wherein sintered titanium dioxide particles are used which have a particle size in the order of 1.0mm to 1.5mm.

(11) AU-B-32980/93
(10) 658472

-2-

7. The process according to any one of claims 1 to 6, wherein titanium dioxide particles are used which have been produced in accordance with the teachings of European patent document EP 265 551.

Our Ref: 452229

658472

P/00/011
Regulation 3:2

AUSTRALIA

Patents Act 1990

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Applicant(s):

Kronos Titan GmbH
Peschstrasse 5
D-5090 Leverkusen 1
GERMANY

Address for Service:

DAVIES COLLISON CAVE
Patent & Trade Mark Attorneys
Level 10, 10 Barrack Street
SYDNEY NSW 2000

Invention Title:

Catalyst for carbonsulfide hydrolysis

The following statement is a full description of this invention, including the best method of performing it known to me:-

CATALYST FOR CARBONYL SULFIDE HYDROLYSIS

The invention relates to a process for the hydrolysis of carbonyl sulfide in a gas mixture, which is passed through a titanium dioxide catalyst at an increased temperature.

During the production of titanium dioxide pigments by vapor-phase oxidation of titanium tetrachloride, the so-called chloride process, ores and slags containing titanium are chlorinated in a reactor in a reducing atmosphere at about 1000°C. Materials containing carbon, for example petroleum coke, are used as reduction agents. The gas mixture which exits the reactor contains, apart from metal chlorides (mainly titanium tetrachloride and iron (III)-chloride) coke, non-cracked ore, silicon dioxide, carbon dioxide, carbon monoxide, nitrogen, hydrogen chloride and, due to the sulphur content in the coke, carbonyl sulfide. Titanium tetrachloride, which has not been completely precipitated, and hydrogen chloride have to be extracted from the gas flow, for example according to the teachings in German patent publication DE-A1-37 42 838. Therefore, due to the content of carbon monoxide the exhaust gas is scorched before it is released into the atmosphere. Carbonyl sulfide is converted into sulfur dioxide and carbon dioxide during the combustion of the waste gas. Furthermore, the sulfur compounds have to be removed from the exhaust gas. It is sensible to perform the de-sulfurization prior to the combustion or scorching of the exhaust gas as the gas amount to be cleansed is then significantly smaller. The de-sulfurization prior to the combustion of the exhaust gas comprises at least two stages:

In a first stage the hydrolysis of the carbonyl sulfide;

and in a further stage the oxidation of hydrogen sulfide to sulfur.

The invention relates to a process of the first stage during the de-sulfurization of the exhaust gas, as removal processes for hydrogen sulfide are well known.

The reaction of carbonyl sulfide (with a COS-component in the gas mixture of up to 0.5% by volume) with water and using a catalyst consisting of aluminium oxide or titanium dioxide is described in the European patent publication EP-A1-215 317. Neutral or slightly alkaline gas mixtures can be de-sulfurized with this process. However, if the gases also contain acid components (for example 1-2 ppm hydrogen chloride and hydrolysis by-products of titanium tetrachloride, which are typically found in exhaust gases from the chloride process) then the reaction speed or rate deteriorates rapidly due to the consumption of the catalyst; the catalyst has to be renewed frequently.

In the US Patents No. 4485189, 4442958, and 4532119 it has been suggested to treat the titanium dioxide with alkaline earth metal sulfates to increase the reaction rate. It has been noticed, however, that the problem, namely, to increase the time period in between replacement of the catalyst when used with gases containing hydrogen chloride, has yet not been solved satisfactorily. This is the reason why the carbonyl sulfide hydrolysis has to be accomplished using the tedious, long known process with activated carbon, which process is described, for example, in the German patent publication DE-A-20 54 016. This process, as well, has problems with regards to the waste management and regeneration of the catalyst.

The present invention seeks to provide a catalyst, which accelerates the reaction of carbonyl sulfide into hydrogen chloride in an acid gas, which catalyst maintains its effectiveness a long time and furthermore can be regenerated in an economical manner.

The invention therefore provides a catalyst of the aforementioned type, which is characterised in that sintered titanium dioxide particles are used. These particles regularly are a by-product of the gaseous phase oxidation of titanium tetrachloride.

5

Further advantageous improvements of the process are described in the dependent claims.

Sintered titanium dioxide particles are known as scrub-solids and are deployed in the chloride process to produce titanium dioxide when the reacting gases have to be cooled by means of indirect heat exchange, because this type of scrub-solids can maintain the cooling surfaces substantially free of deposits. The scrub-solids are a by-product in the chloride process for producing titanium dioxide. The production of scrub-solids is described, for example, in the European patent publication EP-B1-265 551. The process described therein can be regulated in such a way that a larger quantity of scrub-solids can be obtained than would be necessary for the production of pigments. Such scrub-solids consist of sintered titanium dioxide, which has been subjected to a further calcination, and have a particle size of above 0.15 mm, preferably. The basic material of the scrub-solids consist of deposits and crusts which build-up on the side panels or walls of the reacting zone when titanium dioxide is produced using the chloride process by means of oxidising titanium tetrachloride with oxygen in a gaseous phase.

It is surprising that such sintered titanium dioxide particles are precisely and particularly useful in a catalyst process, which takes place on the surface of the particles, as the known titanium dioxide scrub-solids have a relative small specific surface in the region of $2\text{m}^2/\text{g}$.

Particularly preferred are scrub-solids which have



been treated with an alkaline solution prior to calcination so that the alkaline material content in the sintered titanium dioxide particles is in the order of 0.01 to 0.20% by weight sodium hydroxide or 0.01 to 0.30% by weight potassium hydroxide (each in relation to water-free titanium dioxide). It is, however, also possible to use "pure" titanium dioxide scrub-solids for the catalyst; however, a subsequent treatment of the scrub-solids with sodium hydroxide or sodium aluminate, as shall be later described, is envisaged to enhance the cleansing capabilities of the catalyst.

In principle it makes no difference in which one of the large scale technical processes the catalyst for the hydrolysis of carbonyl sulfide is to be used. Ideally, however, the process is to be used in the first stage of the de-sulfurization of chlorinated exhaust gases, if and when ores containing titanium are to be chlorinated in the chlorinating reactor and titanium dioxide pigments are to be produced from titanium chloride. The sintered titanium dioxide particles (scrub-solids), which are to be used as the catalyst, can in this case practically be used in a closed loop process. The used catalyst can either be fed in a known manner into the heat exchanger for cooling the reaction gases produced during the gas-phase oxidation of titanium chloride, where it can accomplish unaltered its function as scrub-particles or, on the other hand, the used catalyst can be fed into the chlorinating reactor, where it basically acts as raw material to be cracked in the reaction and exits the reactor in form of titanium tetrachloride. No problems whatsoever arise during the removal and disposal of the catalyst.

Furthermore, the sintered titanium dioxide particles (scrub-solids), which are used as a catalyst, can be regenerated using a simple process, in that the particles are treated afterwards with sodium hydroxide or

sodium aluminate.

Because the catalytic hydrolysis constitutes a surface reaction type, the catalyst is used in a fluidized bed, in a fixed bed or as a swirl flow layer. The operating temperature preferably is in the range of 100 to 200°C and the contact time in the order of seconds.

The hydrolysis of carbonyl sulfide is especially favourably accelerated if and when the sintered titanium dioxide particles according to the invention have been treated with sodium hydroxide solution - or sodium aluminate solution. Used catalysts can also be reactivated by such a treatment. In the order of about 1% sodium hydroxide, or 2% sodium aluminate, when related to the titanium dioxide particles, have to be applied to the scrub-solids. The treatment with sodium aluminate is more effective than with sodium hydroxide.

The invention shall now be further described in the following examples.

Example 1

An exhaust gas, which is produced during the chlorination of raw-materials containing titanium, has, on use of coke with 1.6% sulfur after separation of the metal chlorides, especially of titanium tetrachloride, and washing-out of the hydrogen chloride a temperature of 30°C and the following composition:

CO	-	42.4	vol.-%
CO ₂	-	30.7	vol.-%
COS	-	0.43	vol.-%
H ₂ S	-	1.0	ppm
H ₂ O	-	4.75	vol.-%
HCl	-	2.0	ppm
TiOCl ₂	-	1.0	ppm
N ₂	-	rest	

4000 Nm³/h of this gas are heated to 2000°C in a tube array heat exchanger and led through a catalyst bed consisting of 6000 l scrub-solids with a particle size of 1-1.5mm. The catalyst is contained in a column (hollow cylinder) with gas-porous side walls with the following dimensions:

outer diameter	1600mm
inner diameter	800mm
column height	4000mm

The converted or processed gas has on its outflow from the catalyst bed the following composition:

CO	-	42.4 vol.-%
CO ₂	-	31.1 vol.-%
COS	-	42 ppm
H ₂ S	-	0.42 vol.-%
H ₂ O	-	4.32 vol.-%
HCl	-	2.0 ppm
TiOCl ₂	-	1.0 ppm
N ₂	-	rest

It is evident from the gas analysis that 99% of the carbonyl sulfide is converted into hydrogen sulfide. After 400h (or 600 h) operating time the turnover or efficiency of conversion is at 98.8% (or 98.5%). The hydrogen sulfide can be extracted from this exhaust gas by washing with solvents based on iron (III) or vanadium (VI) without any difficulty, for example using the LO-CAT or the Stretfort-process.

Example 2

The process applied is essentially the same as in Example 1 but coke with 4.7% sulfur is used instead. The exhaust gas contains now prior to its introduction into the contact apparatus (catalyst filled column) 1.21 vol.-% carbonyl sulfide, which after the conversion is reduced to

112 ppm. This relates to a carbonyl sulfide conversion of about 99%. The carbonyl sulfide conversion reduces to 98.1% after 800h operating time.

5 Example 3

The process applied is essentially the same as in Example 1 with the difference that used scrub-solids (waste product of the carbonyl sulfide conversion when this falls below 90% conversion efficiency are sprayed with a 10% sodium hydroxide solution before use. The amount of sodium hydroxide which is accumulated on the scrub-solids
10 is about 1%, when related to the mass of the titanium dioxide. The carbonyl sulfide conversion remains unchanged at 99.3% immediately after the initiation of the process and after 600h operating time.

A closed-loop cycle for sintered titanium dioxide particles can be achieved. A
15 partial amount of the sintered titanium dioxide particles, which have been separated from the pigment, calcined and normally been treated with alkaline metals, are fed into the contact apparatus. In an especially preferred embodiment, the titanium dioxide particles are sprayed prior to their use with a sodium aluminate solution. The carbonyl sulfide has been converted in excess of 98% into hydrogen sulfide in the exhaust gas leaving the
20 contact apparatus. The hydrogen sulfide can then be oxidised into elementary sulfur using a conventional process in a further apparatus down the production line.

The temperature in the catalyst bed has to exceed 60°C, preferably 80°C. The height of the catalyst bed and the flow-through velocity has to provide for a minimum
25 contact time of no less than 3 sec. The use of titanium dioxide particles with an average particle diameter of 1.0 to 1.5mm is particularly preferred.

As a comparison to the present process, if the exhaust



gas is only treated with water vapour (between 3- and 21-times the stoichometric amount of water) with temperatures around 140°C and without a catalyst, virtually no hydrolytic cracking of carbonyl sulfide can be observed.

It has thus been noticed, that the catalyst according to the present invention can provide for a carbonyl sulfide hydrolysis conversion of about 98% even when coke types with relatively high sulfur content percentages are used and therefore the exhaust gas contains higher amounts of carbonyl sulfide.

The claims defining the present invention are as follows:

1. A process for the hydrolysis of carbonyl sulfide in a gas mixture which is passed through a titanium dioxide catalyst at an increased temperature, wherein sintered titanium dioxide particles are used as the catalyst.
2. The process according to claim 1, wherein titanium dioxide particles are used which are obtained as a by-product in the large-scale technical production of titanium dioxide using the chloride process and which are used as scrub-solids for maintaining the heat transfer during indirect cooling of the reaction gases of the gaseous phase oxidation of titanium tetrachloride.
3. The process according to claim 1 or 2, wherein titanium dioxide particles which have been treated prior to use with a sodium hydroxide solution or a sodium aluminate solution are used for the catalyst.
4. The process according to claim 1, 2 or 3, wherein the temperature of the catalyst is above 60°C.
5. The process according to any one of claims 1 to 4, wherein the temperature of the catalyst is above 80°C.
6. The process according to any one of claims 1 to 5, wherein sintered titanium dioxide particles are used which have a particle size in the order of 1.0mm to 1.5mm.
7. The process according to any one of claims 1 to 6, wherein titanium dioxide particles are used which have been produced in accordance with the teachings of European patent document EP 265 551.
8. The process according to claim 7, wherein the titanium



dioxide particles have been treated using an alkaline solution prior to their calcination.

9. The process according to any of the preceeding claims 1 to 8, wherein the sintered titanium dioxide particles are treated with a sodium hydroxide solution or a sodium aluminate solution for regenerating the catalyst.

10. The process according to any one of the preceeding claims 1 to 9 wherein the content of hydrogen chloride in the gas mixture is held the smallest possible, prior to the contact with the catalyst.

11. A process for the hydrolysis of carbonyl sulfide in a gas mixture which is passed through a titanium dioxide catalyst, substantially as herein described with reference to any one of the examples.

12. A gas mixture from which carbonyl sulfide has been at least partly removed when produced by the process of any one of the preceeding claims.

ABSTRACT

The hydrolysis of carbonyl sulfide is catalytically enhanced by sintered titanium dioxide particles (scrub-solids), which have been mainly used to prevent wall sedimentation during the production of titanium dioxide using the chloride process. It is particularly advantageous that the sintered titanium dioxide particles have been treated with sodium hydroxide or sodium aluminate; the catalyst can also be regenerated by such a treatment.

