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File No.: T 0653/90 - 3.3.2
Application No.: 84 200 720.5
Publication No.: 0 134 594
Classification: C01B 17/04
Title of invention: Process for the oxidation of hydrogen sulphide to
elemental sulphur and/or sulphur dioxide

DECISION
of 6 October 1993

Applicant: -
Proprietor of the patent: Shell Internationale Research Maatschappij B.V.
Opponent: Rhone-Poulenc Chimie

Headword:

EPC: Art. 56

Keyword: "Inventive step (yes)"

Headnote
Catchwords



Case Number: T 0653/90 - 3.3.2

D E C I S I O N
of the Technical Board of Appeal 3.3.2
of 6 October 1993

Appellant: Rhone-Poulenc Chimie
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Decision under appeal: Decision of the Opposition Division of the
European Patent Office dated 10 May 1990, posted
on 15 June 1990 concerning maintenance of European
patent No. 0 134 594 in amended form.

Composition of the Board:

Chairman: P.A.M. Lançon
Members: M.M. Eberhard
E.M.C. Holtz

Summary of Facts and Submissions

- I. European patent No. 0 134 594 based on application No. 84 200 720.5 was granted on the basis of eleven claims.
- II. The Appellant (Opponent) filed a notice of opposition requesting revocation of the patent on the ground of lack of inventive step. During the opposition proceeding the Appellant relied upon the following documents:
- (1) GB-A-769 996
 - (2) EP-A-0 039 266
 - (3bis) Gershingorina A.V, Gerei S.V, Katal. Katal 1978, 16, 59-64, french translation.
- III. By an interlocutory decision the Opposition Division decided to maintain the patent in the form as amended during the oral proceedings held on 10 May 1990. In this decision it was held that the titanium catalysts of the closest prior art, i.e. document (1), had the drawback of giving too high a level of SO₂ emissions and that the solution thereto, namely the use of titanium compounds supported on a silica-containing carrier, was not suggested by documents (2) and (3bis).
- IV. The Appellant lodged an appeal against this decision. An additional document, US-A-4 171 347 (hereinafter document (4)) was cited for the first time in the Statement of Grounds of Appeal.

Oral proceedings were held on 6 October 1993. At the beginning of the proceedings, the question was raised whether Claim 1 submitted on 10 May 1990 meets the requirement of Article 123(2) taking into consideration the fact that the application as originally filed

discloses a temperature range of from 150°C to 350°C for the oxidation of H₂S to SO₂ and from 150°C to 450°C for the oxidation of H₂S to sulphur. In reply thereto the Respondent (Patentee) submitted the following amended Claim 1 as main request:

"A process for the oxidation of hydrogen sulphide in which process a hydrogen sulphide-containing gas is contacted in the presence of a free oxygen-containing gas with a first catalyst composition at a temperature between 150°C and 450°C to form sulphur dioxide or at a temperature between 150° and 350°C to form sulphur dioxide and/or elemental sulphur, wherein the first catalyst composition consists of titanium or a titanium compound on a silica-containing carrier."

V. The Appellant's arguments submitted in writing and at the oral proceedings can be summarised as follows:

Document (1) aimed at reducing the SO₂ emissions and disclosed that this may be achieved by a catalyst consisting of titanyl sulphate deposited on a support, for example activated alumina. Starting from this closest prior art the technical problem to be solved was to reduce further the SO₂ emissions in a process according to (1). In view of the cited prior art it was obvious to the skilled person confronted with this problem to replace the alumina support by a silica support for the following reasons. The problem of the deactivation of the catalysts supported on alumina, i.e. the problem of resistance to sulphation, was well known to the skilled person and document (2) taught the use of a silica support to solve this problem. As shown by document (4), the problem of the resistance to sulphation and the problem of reducing the SO₂ emissions were known to be closely linked together, these two problems representing in fact two equivalent ways of

formulating a more general problem, namely that of the reactivity of the formed SO_2 and of the oxygen at the surface of the catalyst. According to document (4), alumina provided side-reactions which caused either the sulphation of the catalyst or the noxious emission of SO_3 , in contrast to silica supports. Not only alumina but titania was cited in column 9 as sulphatable support. If, as indicated in (4), there was no sulphation with a silica support, then the formation of SO_3 would be greatly reduced and even non-existent. From examples 4, 10 and 11 of document (4), which involved the use of either a V_2O_5 on alumina catalyst or a V_2O_5 on silica catalyst, the skilled person would have inferred that with the former catalyst (examples 4 and 10) sulphur trioxide was produced and subsequently fixed on the alumina whereas with the latter (example 11) SO_3 was not formed at all. Therefore, in view of this teaching the skilled person would have been prompted to use a silica support in the catalyst of document (1) in order to reduce the SO_3 emissions. Even if it could only be deduced from (4) that both the alumina and the silica supports led to about the same result as regards the SO_3 emissions, then it would nevertheless have been obvious to the skilled person to choose a support which does not sulphate, i.e. silica.

The subject-matter of the claims also lacked inventive step in view of documents (1) and (3bis). The latter could not be discarded only because the temperatures were greater than 500°C in order to observe the possible formation of CS_2 . Document (3bis) disclosed that nearly 100% of the hydrogen sulphide was converted to sulphur when the temperature of 500°C was reached. Thus, (3bis) taught that a zirconium catalyst on a silica support was suitable for the catalytic oxidation of H_2S to S and/or SO_2 . As Zr and Ti were considered to be catalytically equivalent in (1), the substitution of

Ti for Zr in the catalyst of (3bis) in order to provide an equivalent titanium catalyst would not have involved an inventive step. The fact that the Respondent had noticed that an obvious catalyst led to low SO₂ emissions in the same oxidation reaction did not constitute a patentable invention but a discovery.

VI. The Respondent put forward i.a. the following arguments:

Document (1) did not disclose a catalyst consisting of titanyl sulphate deposited on a carrier, let alone on an alumina carrier. The statement at page 2, line 44, that "many sulphate catalysts may conveniently be supported on a carrier" clearly implied that not all sulphate catalysts were supported on a carrier. It was said in this document that the titanyl sulphate catalyst took the form initially of unsupported activated titania and this unsupported catalyst was compared with the supported ones. In (1) a preference for an unsupported titanium-containing catalyst was clearly expressed. Therefore (1) pointed away from the invention.

Document (4) did not disclose that the amount of SO₂ produced is less when the catalyst was supported on silica. The teaching of (4) in connection with silica was that this support was resistant to sulphation contrary to alumina but that it presented drawbacks in the presence of water vapour and should not be used in environments containing water vapour. According to (4) the support could be selected from a list of suitable carriers including among others alumina, titania and silica but no preference was given to silica. As regards the SO₂ emissions it was indeed stated in example 11 that no SO₂ was produced, however the oxidation was carried out in the presence of hydrogen. It could not be concluded from table V whether the absence of SO₂ was due to the silica support or to the fact that the

oxidation was performed in the presence of high amounts of hydrogen. In this context document (4) disclosed in column 4 that when the oxidation of H₂S was carried out at temperatures below 900°F with an excess of air the feed gas must contain hydrogen to prevent the formation of SO₃.

The claimed process was also not obvious in the light of the teaching of documents (1) and (3bis) or (1) and (2). Document (3bis) related to the preparation of carbon disulphide and not to the incineration of H₂S. Document (1) neither gave a comparison between zirconium and titanium, nor suggested that these two metals were equivalent catalytic materials for the oxidation of H₂S. In (2), the function of Ti was restricted to the support of a catalyst for the oxidation of H₂S. Zr was considered to be equivalent to Ti only in that it was also used as support.

- VII. The Appellant requested that the decision under appeal be set aside and that the patent be revoked. The Respondent requested that the appeal be dismissed and the patent be maintained in amended form on the basis of claims 1 and 9 as submitted in the oral proceedings, claims 2 to 8 as submitted on 10 May 1990, and the description pages 2, 5 to 10 as appended to the decision under appeal and pages 3 and 4 as submitted in the oral proceedings.

Reasons for the Decision

1. The appeal is admissible.
2. The amendments in the claims and in the description meet the requirements of Article 123(2) and (3). In particular the temperature range of from 150°C to 350° C for the oxidation of H₂S to elemental sulphur is supported by Claim 12 as originally filed and the temperature range of from 150°C to 450°C for the oxidation of H₂S to SO₂ is directly and unambiguously derivable from the original application, page 9, lines 11 to 14, and original Claim 9. The amended claims do not broaden the scope of protection of the granted patent.
3. Document (4) was submitted for the first time by the Appellant at the appeal stage in reply to the Opposition Division's objection that the Appellant had provided no evidence in support of its arguments presented during the oral proceedings (cf. page 5, last paragraph of the decision under appeal and point 5.2 of the Statement of Grounds of Appeal). The Board has examined the relevance of this document and has come to the conclusion that it is more relevant than documents (2) and (3bis) relied upon in the opposition proceeding and that it might have an influence on the outcome of the decision. Therefore, it was decided to take this document into consideration (Article 114(1) EPC).
4. As acknowledged by the Appellant, none of the cited documents discloses the use of a catalyst consisting of a titanium or a titanium compound or a silica-containing carrier in a process for the oxidation of hydrogen sulphide to elemental sulphur and /or sulphur dioxide. Therefore the subject-matter of Claim 1 is novel.

5. The Board considers, in agreement with the parties and the Opposition Division, that document (1) represents the closest prior art.

5.1 This document discloses a process for the oxidation of hydrogen sulphide to sulphur dioxide wherein a H_2S containing gas is contacted with a catalyst in the presence of a free oxygen-containing gas at a temperature between $180^{\circ}C$ and $450^{\circ}C$. The catalyst consists of one or more sulphates of heavy metals or metal oxide cations or of oxides of metals superficially converted to sulphates of metal oxide cations (cf. Claim 1). Nine possible sulphates of heavy metals are recited in Claim 3, and Claim 4 discloses a list of five possible sulphates of metal oxide cations, of which titanyl sulphate. According to Claim 5, which is appended to any of the preceding claims, the catalyst may be supported on a carrier, e.g. activated alumina or granules of fired white china clay. The Appellant has contended that document (1) discloses a titanyl sulphate catalyst supported on a carrier such as alumina, whereas this was contested by the Respondent.

According to the description page 2, lines 44 to 47, **many** sulphate catalysts may conveniently be supported on a carrier, e.g. activated alumina or granules of fire white china clay. In the Board's opinion it follows therefrom that some sulphates may be supported on a carrier and others not. Examples of sulphates of heavy metals supported on alumina are given at page 2, lines 61 to 85. Then, the sulphates of metal oxide cations are considered at page 2, lines 97 to 116. In this passage it is disclosed that vanadyl sulphate may be used supported on alumina. It is further said that other sulphates of the metal oxide cation type, such as **titanyl sulphate**, may conveniently take the form initially of the oxide as porous granules, for example

initially unsupported activated titania. The oxide is then the support for the sulphate to which the more accessible superficial layers are converted during the H₂S oxidation (cf. lines 105 to 109). Therefore, in the case of titanium, the catalyst which is individualised in the description is one consisting of a core of titania and superficial layers of titanyl sulphate, the titania constituting in fact the support for the titanyl sulphate.

A titanyl sulphate catalyst supported on an alumina carrier is not individualised in document (1). As, on the one hand, it is not clearly and unambiguously derivable from (1) that all the sulphate catalysts may be supported on a carrier and, on the other hand, it can be arrived at a titanyl sulphate catalyst on an alumina carrier only by selecting the two starting materials from two lists each comprising several alternatives, this catalyst is not considered to be disclosed in (1) (cf. decision T 12/81, OJ EPO, 1982, 296, points 13 and 14 to 14.2; T 7/86, OJ EPO, 1988, 381, point 5.1). Under these circumstances, the Board considers that the catalytic oxidation of H₂S to SO₂ carried out in the presence of a catalyst consisting of titanyl sulphate on titania as defined above represents the closest prior art.

- 5.2 Starting from this closest prior art, the technical problem underlying the patent in suit can be seen in providing a process for the oxidation of the hydrogen sulphide contained in a gas to sulphur dioxide and/or elemental sulphur, which process leads to a lower SO₂ content in the treated gas.

It is proposed to solve this problem by carrying out the oxidation reaction in the presence of a catalyst consisting of titanium or a titanium compound on a

silica-containing carrier as indicated in Claim 1. A comparison of example 10 of the patent (amended version) with the last comparative experiment shows that by replacing a catalyst consisting of initially unsupported titanium oxide, i.e. a catalyst similar to that involved in the closest prior art, by a catalyst consisting of a titanium compound on a silica carrier the oxidation of the hydrogen sulphide contained in the feed gas leads to substantially lower SO₂ emissions (<5 ppmv instead of 50 ppmv) under identical operating conditions. In view of these results, it is credible that the technical problem has been really solved by the claimed process.

5.3 Document (1) itself is also concerned with the problem of maintaining the concentration of the sulphur trioxide in the treated gas at a low level. This problem is solved in (1) by performing the oxidation of H₂S to SO₂ at a temperature between 180°C to 450°C in the presence of the specific catalysts disclosed therein (cf. page 1, lines 51 to 69 and 77 to 84 and page 2, lines 1 to 9). However, this document contains no information as to how the SO₂ concentrations in the treated gas might be further reduced. Moreover, as a silica or a silica-containing carrier is not mentioned in (1), this document could not give the skilled person an incentive to perform the catalytic oxidation in the presence of a catalyst consisting of titanium or a titanium compound on a silica-containing carrier in order to solve the problem defined above.

5.4 Document (4) discloses a process for the oxidation of H₂S to SO₂ in a feed gas containing H₂S and a substantial proportion of at least one secondary oxidizable component selected from H₂, CO and light hydrocarbons. The feed gas is contacted in the presence of air or oxygen with an oxidation catalyst at temperatures between 300 and 900°F (149 to 482°C), the catalyst

comprising vanadium oxide and/or sulphide supported on a non-alkaline porous refractory oxide (cf. Abstract and Claim 1). The preferred catalyst comprises between 5-15 wt% V_2O_5 on hydrogen mordenite or alumina. This process makes it possible selectively to oxidise H_2S to SO_2 in the presence of normally oxidisable components such as H_2 , CO , light hydrocarbons or ammonia without oxidising these components even when excess air is used to perform the conversion to SO_2 . Also no detectable amount of SO_3 is formed when hydrogen is a component of the feed gas or, in the absence of hydrogen, when temperatures below about $500^\circ F$ ($260^\circ C$) are used (cf. Abstract; column, 2, lines 52 to 62; column 2, lines 5 to 24). A list of at least twenty suitable non-alkaline supports is given in column 8, lines 42 to 68. In the examples of (4), the supports for the vanadium oxide catalysts are hydrogen mordenite, alumina, silica, aluminium phosphate, or a mixture of silica and hydrogen mordenite.

Document (4) further teaches that hydrogen mordenite has the advantage of being resistant both to sulphation and to attack by water vapour and that silica does not sulphate but is susceptible to decomposition and volatilisation in the presence of water vapour (cf. column 9). It is also indicated in column 9 (lines 13 to 37) that alumina based catalysts appear to be susceptible to sulphation and consequent gradual deactivation in the presence of excessive amounts of SO_2 and O_2 , the sulphation resulting from the reaction of SO_2 and O_2 on the catalyst surface either directly or indirectly via the intermediate formation of SO_3 . Vanadium oxide catalysts supported on titania, silica-titania, zirconia, silica-magnesia etc. are also said to be sulphatable. In connection with the sulphation of the V_2O_5 on alumina catalyst it is also referred to examples 4 and 10. Example 10 shows that the alumina based catalyst contains more sulphur in the form of sulphates

than the mordenite based catalyst and, therefore, that it is less resistant to sulphation. However, this example gives no information as to the concentration of SO_3 in the treated gases. Data about the SO_3 concentration are given for the V_2O_5 on alumina catalyst of example 4. It is reported that no SO_3 was found in the treated gas and essentially no SO_3 was formed at temperatures below about 900°F (482°C) (cf. column 12, lines 38 to 45, and column 16, lines 48 to 54). In example 11, the oxidation of a feed gas containing similar amounts of hydrogen, CH_4 , O_2 and H_2S as the feed gas of example 4 was carried out in the presence of a V_2O_5 on silica catalyst. The results as regards the SO_3 production at temperatures below 900°F and the amount of SO_3 in the final gas are similar to those of example 4. Therefore, it cannot be inferred from this teaching that by replacing a sulphatable support by a non-sulphatable one such as silica, the concentration of SO_3 in the treated gases would be lower.

Moreover, it is pointed out in column 4 (lines 8 to 25) that the use of excess air in the presence of the vanadia catalyst does not result in the production of SO_3 provided that the feed gas contains a certain amount of hydrogen. In the absence of hydrogen in the feed gas either the operating temperature should be maintained below about 500°F (260°C), or only 0.8 to 1.05 times the stoichiometric amount of air should be fed, or H_2 should be blended with the air fed to prevent the formation of more than about 100 ppmv of SO_3 . Therefore, (4) clearly teaches that parameters like the presence of hydrogen, the relative amounts of O_2 and H_2S and the temperature have an influence on the SO_3 formation but does not suggest that the nature of the support might decrease the concentration of SO_3 in the treated gases. It follows that in view of the teaching of (4) the skilled person confronted with the problem stated above would

not contemplate using a catalyst consisting of a titanium compound supported on a silica-containing carrier instead of titanyl sulphate on titania since he could not expect that this substitution of the support would lead to a decrease of the SO₃ content in the treated gases (cf. T 2/83, OJ EPO 1984, 265).

5.5 The Appellant's argument that even without expectation of an improvement as regards the SO₃ emissions it would be obvious to the skilled person to use a silica support in the catalyst of (1) in view of its resistance to sulphation, is not convincing. It is based on the assumption that the titanyl sulphate on titania catalyst of (1) is not resistant to sulphation and that two partial problems had to be solved, namely lowering the SO₃ concentration in the treated gas and preventing the catalyst sulphation. However as, on the one hand, this assumption is not supported by any evidence and on the other hand, it is neither derivable from the patent in suit nor from the file that the titanyl sulphate on titania catalyst of (1) sulphates rapidly under the operating conditions used in this document, the Board cannot agree with this argument. In this context, it is observed that the V₂O₅ on alumina catalyst of (4) is susceptible to sulphation only under certain operating conditions (cf. column 9, lines 12 to 41). Furthermore, the catalysts disclosed in document (2) for the same reaction of oxidation of H₂S to SO₂ are supported on titania or silica-titania and are said to exhibit an excellent life period. Thus, it can neither be derived from the information in (4) nor from that in (2) that preventing the catalyst sulphation was a problem to be solved starting from the closest prior art defined above.

- 5.6 At the oral proceedings the Appellant did not rely any more upon the remaining documents (2) and (3bis) in connection with inventive step.

Document (2) also relates to a process for the oxidation of H_2S to SO_2 in the presence of a catalyst. The catalysts disclosed here contain a support selected from titania, silica, zirconia, silica-magnesia, silica-zirconia, silica-titania, zirconia-titania or a zeolite and at least one catalytically active component selected from the list reported at page 10, lines 10 to 15 (cf. claims 15 and 1, examples). This list includes neither titanium nor a titanium compound. As document (2) is not concerned with the problem of reducing the SO_3 concentration in the treated gas and does not give any information about the SO_3 content thereof, it cannot give the skilled person an incentive to use a silica support instead of titanium oxide in the catalyst of (1) in order to decrease the SO_3 emissions.

- 5.7 Document (3bis) discloses that when a feed gas comprising CH_4 , H_2S and O_2 is contacted with a catalyst consisting of ZrS_2 on silica, the oxidation of the methane to carbon oxides begins at about $500^\circ C$ and the H_2S conversion at this temperature is close to 100%. Reference is made in this respect to table 1 which shows a H_2S conversion of 87% and 88.5% at $495^\circ C$ and $507^\circ C$ respectively with two catalysts of different Zr contents (cf. page 3, lines 7 to 11 and table 1). As this document neither relates to the oxidation of H_2S to SO_2 at temperatures between 150 and $450^\circ C$ nor deals with the problem of decreasing the formation of SO_3 , it would be of no assistance to the skilled person faced with the problem stated above. The Appellant's arguments as regards the substitution of Ti for Zr in the catalyst of (3bis) in order to provide an equivalent titanium catalyst are not convincing since the closest prior art

is not document (3bis) but document (1) (this was not contested by the Appellant) and the problem to solve starting from document (1) is not to provide an equivalent catalyst.

5.8 For the reasons given above, it was not obvious to arrive at the claimed process in view of the cited prior art. Therefore, the subject-matter of Claim 1 is considered to meet the requirements of inventive step.

6. The dependent Claims 2 to 9 which relate to preferred embodiments of Claim 1 derive their patentability from that of Claim 1.

Order

For these reasons, it is decided that:

1. The appeal is dismissed.
2. The decision under appeal is set aside.
3. The case is remitted to the first instance with the order to maintain the patent in amended form on the basis of the following documents:
 - Claims 1 and 9 submitted in the oral proceedings,
 - Claims 2 to 8 submitted on 10 May 1990,
 - the description, pages 2 and 5 to 10, as appended to the decision under appeal, and
 - the description, pages 3 and 4, as submitted in the oral proceedings.

The Registrar:



P. Martorana

The Chairman:



P.A.M. Lançon

M. Fl.
W