

Internal distribution code:

- (A) [] Publication in OJ
(B) [] To Chairmen and Members
(C) [X] To Chairmen
(D) [] No distribution

**Datasheet for the decision
of 25 July 2006**

Case Number: T 0990/01 - 3.3.07

Application Number: 93909144.3

Publication Number: 0688243

IPC: B01J 23/52

Language of the proceedings: EN

Title of invention:

Pretreatment of palladium-gold catalysts useful in vinyl acetate synthesis

Patentee:

MILLENNIUM PETROCHEMICALS, INC.

Opponents:

Celanese Chemicals Europe GmbH

Headword:

-

Relevant legal provisions:

EPC Art. 123(2)

Keyword:

"Disclaimer - disclosed in the application as filed (no) - based on an accidental anticipation (no) - allowable (no)"

Decisions cited:

G 0001/03

Catchword:

-



Case Number: T 0990/01 - 3.3.07

D E C I S I O N
of the Technical Board of Appeal 3.3.07
of 25 July 2006

Appellants: MILLENNIUM PETROCHEMICALS, INC.
(Patent Proprietors) 11500 Northlake Drive
Cincinnati, Ohio 45249 (US)

Representative: Grünecker, Kinkeldey,
Stockmair & Schwanhäusser
Anwaltssozietät
Maximilianstrasse 58
D-80538 München (DE)

Respondents: Celanese Chemicals Europe GmbH
(Opponents) Werk Ruhrchemie
Patentreferat
Postfach 14 02 37
D-46147 Oberhausen (DE)

Representative: -

Decision under appeal: Decision of the Opposition Division of the
European Patent Office posted 29 June 2001
revoking European patent No. 0688243 pursuant
to Article 102(1) EPC.

Composition of the Board:

Chairman: S. Perryman
Members: B. Struif
G. Santavicca

Summary of Facts and Submissions

I. The mention of the grant of European patent No. 0 688 243 on European patent application No. 93 909 144.3 filed on 15 March 1993 was published on 8 July 1998. The patent was granted with fifteen claims. The only independent claim read as follows:

"1. A method for the pretreatment of a catalyst, the method comprising in sequence:

heating a virgin catalyst comprising metallic palladium and gold, for at least 15 minutes at a temperature at least sufficient to partially oxidize the palladium, in the presence of an oxidizing agent selected from the group consisting of oxygen, nitrogen oxides, nitrate salts, hydrogen peroxide and an oxygen containing gas; withdrawing the oxidizing agent and introducing an inert gas, and treating the catalyst at a temperature up to 500°C for at least 15 minutes in the presence of a reducing agent."

II. A notice of opposition was filed against the granted patent, in which revocation of the patent in its entirety was requested on the grounds of Article 100(a) EPC with respect to lack of novelty and lack of an inventive step, respectively. The opposition was supported *inter alia* by the following documents:

D1: CA-A- 820 352

D2: US-A-4 490 481

III. By a decision posted on 29 June 2001, the opposition division revoked the patent. That decision was based on a set of claims 1 to 12 submitted with letter of 19 September 2000 as the main request and on two auxiliary requests submitted at the oral proceedings before the opposition division. Claim 1 of the main request had the following version:

"A method for the pretreatment of a catalyst, the method comprising the sequential steps of:

- heating a virgin catalyst comprising metallic palladium and gold for at least 15 minutes at a temperature at least sufficient to partially oxidize the palladium in the presence of an oxidizing agent selected from the group consisting of oxygen, nitrogen oxides, nitrate salts, hydrogen peroxide and an oxygen containing gas;
- withdrawing the oxidizing agent and introducing an inert gas, and
- treating the catalyst at a temperature up to 350°C for at least 15 minutes in the presence of hydrogen;

provided that the virgin catalyst does not contain gold in an amount of 0.003 to 0.3% by weight."

Claim 1 of the first auxiliary request read as follows:

"A method for the pretreatment of a catalyst, comprising the sequential steps of:

- heating a virgin catalyst comprising metallic palladium and gold for at least 15 minutes at a temperature at least sufficient to partially oxidize the palladium in the presence of an oxidizing agent selected from the group consisting of oxygen, nitrogen oxides, nitrate salts, hydrogen peroxide and an oxygen containing gas;
- withdrawing the oxidizing agent and introducing an inert gas, and
- treating the catalyst at a temperature up to 350°C for at least 15 minutes in the presence of a hydrogen;

and comprising the additional step of

introducing a reaction mixture comprising ethylene, acetic acid and oxygen following the hydrogen."

Claim 1 of the second auxiliary request differed from claim 1 of the first auxiliary request in that after the term "in the presence of hydrogen" the following feature was introduced:

", wherein hydrogen is introduced when the catalyst is at ambient temperature"

IV. The opposition division held *inter alia* that:

- (a) Due to the disclaimer at the end of claim 1 of the main request, the subject-matter of that request was novel over D2. D2 concerned a catalyst for the selective hydrogenation of diolefinic and/or

acetylenic hydrocarbons and not a catalyst for a vinyl acetate synthesis which proceeded via a completely different reaction mechanism. Thus, D2 was an accidental anticipation, not relevant for assessing inventive step. Hence, the disclaimer based thereon was allowable.

(b) The claimed subject-matter of the main and the auxiliary requests did not involve an inventive step, when starting from D1 as the closest state of the art.

V. On 5 September 2001, the proprietors (appellants) filed a notice of appeal against the above decision. In the statement setting out the grounds of appeal filed on 29 October 2001, the appellants submitted a set of claims 1 to 12 as main request and one auxiliary request. Claim 1 of the main request read as follows:

"A method for the pretreatment of a virgin catalyst comprising the sequential steps of:

- heating a virgin catalyst comprising metallic palladium and gold, not previously used in catalyzing a reaction, for at least 15 minutes at a temperature at least sufficient to partially oxidize the palladium in the presence of an oxidizing agent selected from the group consisting of oxygen, nitrogen oxides, nitrate salts, hydrogen peroxide and an oxygen-containing gas;
- withdrawing the oxidizing agent and introducing an inert gas, and

- treating the oxidized product at a temperature of up to 350°C for at least 15 minutes in the presence of hydrogen;

with the proviso that the virgin catalyst does not contain gold in an amount of 0.003 to 0.3% by weight."

Claim 1 of the auxiliary request read as follows:

"A method for the pretreatment of a catalyst comprising the sequential steps of:

- heating a virgin catalyst comprising metallic palladium and gold for at least 15 minutes at a temperature of from 125 to 350°C in the presence of an oxidizing agent selected from the group consisting of oxygen, nitrogen oxides, nitrate salts, hydrogen peroxide and an oxygen-containing gas;
- withdrawing the oxidizing agent and introducing an inert gas, and
- treating the oxidized product at a temperature up to 350°C for at least 15 minutes in the presence of hydrogen,

with the proviso that the virgin catalyst does not contain gold in an amount of 0.003 to 0.3% by weight."

VI. During the appeal proceedings, the respondents (opponents) submitted with letter of 6 March 2003 *inter alia* the following document:

D11: Kirk-Othmer, Encyclopedia of Chemical Technology, John Wiley & Sons, third edition (1980), vol. 11, page 989

- VII. In a communication dated 20 April 2006, the board indicated the points to be discussed during the oral proceedings and in particular addressed the allowability of the disclaimer in the requests on file in view of the decision G 1/03 (OJ EPO, 2004, 413).
- VIII. Oral proceedings were held on 25 July 2006 in the absence of the appellants, who had informed the board by the letter of 9 June 2006 that he would not be attending the oral proceedings (Rule 71(2) EPC).
- IX. The appellants did not reply to the communication of the board, in particular to the question of allowability of the disclaimer of claim 1 in the main and auxiliary request.
- X. The respondents argued in substance as follows:
- The disclaimer in both requests had no basis in the application as filed so that the content of the application as filed had been extended. The claimed subject-matter and D2 concerned a palladium/gold catalyst, which was subjected to a pretreatment by a sequence of an oxidation and a reduction step. The pretreatment of a virgin palladium/gold catalyst was illustrated in examples 1 and 8 of D2 and showed that the oxidation and reduction conditions as claimed were conventional. D11 disclosed that Pd/Au catalysts were suitable for a variety of reactions. Although the use of the catalysts mentioned in D2 was different from the

use described in the patent in suit, the claimed subject-matter was not restricted to any such use, so that the pretreated Pd/Au catalysts could be used in a wide technical field. Hence, the claimed subject-matter did not concern a technical field and purpose remote from that of the catalysts of D2. Consequently, the skilled person would consider D2 when seeking to solve the problem underlying the invention. Thus, D2 was no accidental anticipation in the meaning of G 01/03 (*supra*) and the disclaimer did not comply with Article 123(2) EPC.

XI. The appellants had requested in writing that the decision under appeal be set aside and that the patent be maintained on the basis of the claims of the main request or of the auxiliary request, both filed on 29 October 2001.

XII. The respondents requested that the appeal be dismissed.

Reasons for the Decision

1. The appeal is admissible.

Main request

Amendments to the claims (Article 123 (2) EPC)

2. Claim 1 of the main request contains the following amendment compared to claim 1 as granted, to distinguish the claimed subject-matter from the disclosure of D2:

- "with the proviso that the virgin catalyst does not contain gold in an amount of from 0.003 to 0.3% by weight."

- 2.1 The Board in its communication dated 20 April 2006 raised the question of the allowability of that amendment in view of decision G 1/03 (*supra*). The appellant did not address that objection whilst the respondent at the oral proceedings objected to that amendment.

- 2.2 The first question to be answered is whether or not that amendment has a basis in the application as filed.

- 2.3 The claims as originally filed do not specify any composition of the metallic components of the virgin catalyst. According to the description of the application as filed, the catalyst to be pretreated comprises palladium in an amount of 0.1 to 5 percent and gold in an amount of 0.1 to 2 percent, both based on the weight of the completed catalyst including the support material (page 3, last paragraph). The examples as filed use a catalyst comprising 0.5% by weight of gold and 1% by weight of palladium (page 6, lines 24 to 26). There is no other disclosure in the application as filed, in which the amounts of the metallic components in the catalyst composition is further specified. Thus, the disclaimed amount of 0.003 to 0.3% by weight of gold has no basis in the application as filed.

- 2.4 According to decision G 1/03, a disclaimer may be allowable in order to restore novelty by delimiting a claim against an accidental anticipation under

Article 54(2) EPC; an anticipation is accidental if it is so unrelated and remote from the claimed invention that the person skilled in the art would never have taken it into consideration when making the invention (Order 2.1).

- 2.5 D2, which is a state of the art under Article 54(2) EPC, discloses a catalyst produced by a process consisting essentially of the sequential steps of: admixing a palladium compound with an inorganic carrier, roasting in the presence of an oxygen-containing gas, treating with a reducing agent, admixing a halogenated gold compound with the resultant composition, treating with a reducing agent, washing with an aqueous solution of a compound having a basic reaction so as to lower the halogen content of the catalyst below 10 ppm by weight, and roasting in the presence of an oxygen-containing gas, the palladium and gold compounds being used in amounts such that the resultant catalyst contains 0.03 to 1% palladium and 0.003 to 0.3% gold by weight (claim 1).

The roasting in the presence of oxygen, for example in the presence of air, may be conducted at 100 to 500°C, preferably at 250 to 350°C. Reductions with hydrogen may be conducted at 100 to 400°C, preferably 150 to 300°C (column 3, lines 31 to 39).

- 2.6 According to example 1, three catalysts (A), (B) and (C) are produced. Catalyst (A) is prepared as follows: a carrier is dipped in a solution of palladium acetylacetonate solution, the amount of which being suitable to obtain a final catalyst with a 0.2% by weight content of this metal. The supernatant solution

is removed and the catalyst is dried. Then the catalyst is maintained in a furnace in an air stream at 300°C for 2 hours. In the same furnace, the air is scavenged by nitrogen and then replaced by a hydrogen stream which scavenges the catalyst for 2 hours at a temperature of 300°C. Catalyst (A) is thus obtained.

- 2.6.1 A sample of catalyst (A) is then dipped in an aqueous solution of tetrachloroauric acid as to obtain a final catalyst having a 0.02% by weight gold content. The supernatant solution is removed and the catalyst is then dried, roasted and reduced in the same manner as the palladium catalyst (A). The so-prepared catalyst contains 110 ppm by weight of chlorine and constitutes the catalyst (B).
- 2.6.2 A portion of catalyst (B) is then washed with a solution of NH_4OH to remove chlorine almost completely. The catalyst is then dried, roasted and reduced under the same conditions as the palladium catalyst (A). There is thus obtained catalyst (C) having a chlorine content lower than 10 ppm by weight.
- 2.6.3 A process similar to the preparation of catalyst (C) in example 1 is described in example 8 for the preparation of catalyst (D). In that example the conditions for drying, roasting and reducing are identical to those specified in example 1 except for the temperature of the final reduction with hydrogen, which is effected at 150°C.
- 2.6.4 Catalyst (B) of example 1 of D2 is already a final catalyst in its reduced metallic form, since X-ray analysis indicates the presence of bimetallic

palladium-gold particles in the catalyst (column 4, lines 1 to 4). Furthermore, catalyst (B) can be used afterwards in a catalytic process (table 1). Thus, catalyst (B) is a virgin catalyst in line with the patent in suit (page 2, lines 48 and 49). According to example 1, catalyst (C) is produced by heating the virgin catalyst (B), which contains metallic palladium and gold, and has not been previously used in a catalytic reaction, **in the presence of an oxygen containing gas (air) for at least 15 min (2 hours), which is withdrawn by introducing an inert gas (the air is scavenged by nitrogen) and then treated for at least 15 minutes (2h) at a temperature of up to 350°C (300°C) in the presence of hydrogen (hydrogen stream)** (the conditions in bold refer to the conditions of claim 1 of the main request, whilst the conditions in brackets refer to the conditions in example 1 of D2). The modified conditions of example 8 of D2 for producing catalyst (D) also overlap with those as claimed (point 2.6.3).

2.6.5 From the above analysis it follows that the exemplified catalysts (C) and (D) of D2 are produced by pretreating a virgin metallic palladium/gold catalyst by using the same process steps as now claimed. Thus, the only difference of the claimed subject-matter from that of D2 is the disclaimed range of gold in an amount of 0.003 to 0.3% by weight in claim 1 of the main request, since otherwise the claimed subject-matter would not be novel.

2.7 The process for the pretreatment of a virgin metallic palladium/gold catalyst (B) according to D2 concerns the same technical field as the patent in suit, which

is directed to a method for pretreating a metallic palladium-gold catalyst not previously used by sequential oxidation and reduction steps (page 2, lines 3 and 4).

2.7.1 Furthermore, according to D2 "before use it is convenient to effect a reduction by one of the known methods for examples by means of a hydrogen at temperature from 100 to 400°C, preferably from 150 to 250°C" (column 3, lines 63 to 66). Thus, a reduction by means of hydrogen is a convenient practice "before use" of palladium/gold catalysts. In the light of examples 1 and 8 of D2, it is apparent that the conditions specified therein also cover a reduction with hydrogen after roasting, so that the skilled person would consider those steps as convenient means for making the catalyst suitable before use. Consequently, the process steps of D2 have a purpose similar to that of the patent in suit, namely to make the catalyst suitable for a catalytic reaction.

2.7.2 From the above it follows that the disclosure of D2 which concerns Pd/Au catalysts produced as defined in claim 1 in suit, is neither unrelated nor remote from the claimed invention so that the skilled person would consider that prior art process when seeking to solve any problem to which the present invention can be considered as a solution. Hence, the anticipation of D2 cannot be considered as being accidental in the meaning of G 1/03 (*supra*).

2.8 According to the decision under appeal, the opposition division was of the opinion that D2 concerned a catalyst for selective hydrogenation of diolefinic

and/or acetylenic hydrocarbons whilst the claimed subject-matter seeks to improve a catalyst for vinyl acetate synthesis, so that the disclosure of D2 had to be considered as an accidental anticipation.

2.8.1 The object of D2 concerns the preparation of a catalyst having simultaneously a high resistance to poisoning by sulfur, a high stability with respect to elution by vinylacetylene, as well as a low tendency to oligomers formation (D2, column 2, lines 64 to 68) by avoiding the presence of chlorine in the final catalyst in order to provide a satisfactory activity of these catalysts (column 2, lines 60 and 61). Whilst these different objects are illustrated in the examples, it is not specified what precise effect the final roasting and reducing steps of catalyst (C) and (D) have on the catalyst properties. Since these steps are not only disclosed in the exemplified embodiments (column 4, lines 52 to 55 and column 7, lines 64 to 67) but also in the general description (column 3, lines 31 to 39) and as part of convenient pretreating steps before use (point 2.7.1 above), it can be concluded that these steps generally represent appropriate catalyst forming conditions.

2.8.2 The object of the patent in suit is to achieve a catalyst with improved initial selectivity to vinyl acetate while maintaining a high conversion. It is also an object to reduce the frequency of regeneration or replacement of the catalyst (page 2, lines 27 and 28).

2.9 However, claim 1 as amended concerns a process for the pretreatment of a catalyst before it is used in a catalytic process without any reference to a specific

use. Hence, the catalysts obtained by the process of claim 1 can also be used in a catalytic reaction other than the vinyl acetate synthesis, for example in hydrogenation processes disclosed in D2 and vice versa.

2.10 Although in D2 the specific objects and the use of the catalysts in specific catalytic reactions are different from those particularly specified in the patent in suit, the claims of D2 are not restricted to any such specific use. The present claims are not restricted to a catalyst for use in vinyl acetate synthesis either, so that the intended use does not provide any distinction of the subject-matter of the claims over D2.

2.10.1 According to a Kirk-Othmer's Encyclopedia (D11), a handbook, which relates to the general knowledge of the skilled person, palladium/gold catalyst can be used in hydrogenation, isomerisation, hydrocracking, reforming and partial oxidation of olefins, although the only commercial use of such catalysts is in the manufacture of vinyl acetate (page 989, penultimate sentence in the second full paragraph). Thus, gold/palladium catalysts may be used in technical fields which concern catalytic reactions of organic compounds, which may even use similar starting materials such as ethylene (patent in suit) and diolefinic materials (D2). Consequently, having regard to the claimed context, such specific uses cannot be considered as unrelated or so remote from each other that the skilled person would never have taken D2 into consideration when making the invention.

2.10.2 Even the decision under appeal considered D2 as a relevant state of the art when evaluating (denying)

inventive step, where in section 5.2 at the end thereof it reads: "Moreover, hydrogen is one of the most common reducing agent used in catalyst preparation usually at temperatures between 100 to 300°C (see D2 or D8). Therefore, there is no inventive step (Art. 56 EPC)". Prior art (D2), which is considered as relevant for denying inventive step cannot be an anticipation which "has nothing to do with the invention" (G 1/03, *supra*, section 2.3.4). This reason is confirmed by a further passage of decision G 1/03, according to which "the fact that a document (here D2) is not considered to be the closest prior art is not sufficient to accept an accidental anticipation (section 2.2.2). Furthermore, any argument that the reactions specifically used in D2 (selective hydrogenation of diolefinic and/or acetylenic hydrocarbons) and the patent in suit (vinyl acetate synthesis) follow different reaction mechanisms and that therefore D2 can be treated as an accidental anticipation, ignores that the disclosure of D2 and the claims of the patent in suit are not restricted to any such uses. Consequently, the above argument is neither convincing nor in line with the decision G 1/03 (*supra*).

Auxiliary request

3. Claim 1 of the auxiliary request contains a disclaimer identical to that of claim 1 of the main request so that the same considerations developed under sections 2 to 2.8 above apply *mutatis mutandis* to the auxiliary request as well.
4. From the above it follows that, the disclaimed, non-originally disclosed subject-matter of the main and the auxiliary request is not based on an accidental

anticipation (D2) in the meaning of the decision G 1/03. Hence, the disclaimer contravenes Article 123(2) EPC. Consequently, none of the requests is allowable.

5. In view of the above reasons, it is not necessary to decide whether or not the disclaimer has been properly drafted in accordance with the decision G 1/03 (Headnote II.2).

Order

For these reasons it is decided that:

The appeal is dismissed.

The Registrar

The Chairman

C. Eickhoff

S. Perryman