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D E C I S I O N
of 9 February 1999

Case Number: T 0365/94 - 3.3.2

Application Number: 89113636.8

Publication Number: 0352715

IPC: B01J 21/06

Language of the proceedings: EN

Title of invention:
Twice-aged porous inorganic oxide, catalysts, and polymerization processes

Applicant:
Phillips Petroleum Company

Opponent:
-

Headword:
Twice aging/PHILLIPS

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step (yes)"

Decisions cited:
-

Catchword:
-

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Beschwerdekammern | Boards of Appeal | Chambres de recours

Case Number: T 0365/94 - 3.3.2

D E C I S I O N
of the Technical Board of Appeal 3.3.2
of 9 February 1999

Appellant: Phillips Petroleum Company
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Decision under appeal: **Decision of the Examining Division of the European Patent Office posted 15 November 1993 refusing European patent application No. 89 113 636.8 pursuant to Article 97(1) EPC.**

Composition of the Board:

Chairman: P. A. M. Lançon
Members: M. M. Eberhard
J. H. van Moer

Summary of Facts and Submissions

I. European patent application No. 89 113 636.8 was refused by a decision of the Examining Division. The decision was based on amended claims 1 to 17 according to the main request filed on 14 October 1993.

II. The ground for the refusal was that the subject-matter of amended claim 1 did not involve an inventive step over the disclosure of US-A-3 887 494 (hereinafter D1). According to the decision, the claimed process differed from the process of D1 in that two aging steps are performed instead of one aging step at a pH of from 3 to 9. The Examining Division held that this difference lacked an inventive step in the alternative where step (d) involved spray-drying since it had not been shown that this alternative solved the technical problem of the application. The pore volume of the spray-dried catalyst was only slightly increased over that of an oven-dried catalyst, and a process wherein the hydrogel was oven-dried did not solve the technical problem of the application.

III. The Appellant lodged an appeal against this decision and filed a statement of grounds of appeal in due time. In a communication from the Board, the Appellant was invited to give further information about the technical problem solved by the "spray-drying alternative" of claim 1, starting from D1 as closest prior art. In reply thereto the Appellant filed comparative examples on 14 May 1998, as well as an amended claim 1 comprising an additional embodiment for the drying step (d), ie "oven-drying".

Oral proceedings were held on 9 February 1998. At the oral proceedings the Appellant filed amended claims 1 to 17, as a single request, by way of replacement for all the previous requests. He also submitted additional results concerning the comparative examples of 14 May 1998.

Claim 1 of the said single request reads as follows:

"1. A process to make a porous inorganic oxide comprising the steps of:

a) forming a silica-titania cogel hydrogel by coprecipitating a titanium compound with silica;

b) aging said cogel under substantially neutral pH conditions at a pH of 5 to 8, however, excluding a pH of 8, and at a temperature of 15° to 95°C for a time of at least 1 hour;

c) aging the said neutral-aged cogel under alkaline pH conditions in an aqueous solution with a pH in the range of 8 to 12 pH units, for a time in the range of 1 to 50 hours, at a temperature in the range of 70° to 120°C; and

d) drying the thus twice-aged cogel to form a xerogel by oven drying, by spray-drying or by azeotrope drying."

IV. The Appellant's arguments can be summarised as follows:

Concerning the allowability of the amendments in claim 1, the Appellant referred to decision T 154/88

and argued that run 103 showed poor productivity but did not prove that the oven-dried catalyst gave poor polymerisation productivity in general. It was directly and unambiguously derivable from runs 105, 203 and 305 of Tables 1 to 3 that a twice-aged, oven-dried catalyst solved the problem stated in the description. These runs showed the advantages of the said catalyst over once-aged, oven-dried catalysts regarding surface area, pore volume, pore radius, productivity, melt index and high load melt index (HLMI), no matter whether the twice-aged catalyst was used as such, contained a surfactant, or was alcohol-washed.

Regarding the inventive step issue, it was argued that a comparison between twice-aged, oven-dried catalysts of the invention and once-aged, azeotrope-dried catalysts of D1 was not significant because the respective catalysts were produced by processes differing from each other by two main steps. A comparison of run 101 with run 105 showed that oven-drying did not destroy the pore structure but led, in combination with twice aging, to improved catalysts, ie to a decrease of the surface area and an increase of the pore volume and pore radius. Starting from D1, the technical problem was to provide a method which avoided the use of the expensive azeotrope-drying while giving a catalyst with sufficient activity. Although the results obtained with oven-drying were not as good as with spray-drying or azeotrope-drying, the catalyst had nevertheless a satisfactory performance even in the absence of a surfactant or washing step with alcohol. Table 1 showed that by optimising the operating conditions a catalyst having a good polymer productivity could be obtained.

As regards the twice-aged, spray-dried catalysts, the comparative examples submitted on 14 May 1998 and at the oral proceedings confirmed that they exhibited a higher pore volume and a lower surface area than the once-aged, spray-dried catalysts and gave polymers having improved HLMI and tear resistance. Furthermore, one of the advantages of spray-drying was the significant cost reduction compared to a process in which the much more expensive azeotrope-drying had to be applied in order to obtain a catalyst having a satisfactory performance. It was not decisive whether the twice-aged and spray-dried catalysts were worse or better than the catalysts of D1, which were dried in a completely different way, since the invention clearly lay in the introduction of the second aging step.

V. The Appellant requested that the decision under appeal be set aside and that a patent be granted with amended claims 1 to 17 according to the single request submitted at the oral proceedings.

Reasons for the Decision

1. The appeal is admissible.

2. Amended claims 1 to 17 meet the requirements of Article 123(2) EPC. Claim 1 is based on the combination of original claims 1 and 19 with additional features of the description as originally filed. The original description discloses on page 3, line 32, that the titanium compound must be coprecipitated with the silica. The operating conditions used in steps (b) and

(c) are indicated on page 5, lines 4 to 9, and lines 22 to 28 respectively. It is directly and unambiguously derivable from the description as filed that step (b) is carried out at a pH lower than the pH of the second aging step, ie lower than 8. Oven-drying is not mentioned as a possible method for drying the twice-aged hydrogel in the more general part of the description (ie pages 2 to 11). However, it is directly and unambiguously derivable from Tables 1 to 3 on pages 13, 14 and 15 that a process comprising twice aging the hydrogel under the claimed operating conditions and oven-drying the resulting gel may lead to a catalyst having a higher average pore radius and/or a higher pore volume than a catalyst prepared by once aging and oven-drying. Thus, it is implicit from the original description that the objective stated on page 2, lines 29 to 32, of the description can also be achieved when the hydrogel is oven-dried, and therefore, that oven-drying also represents an embodiment according to the invention.

The features of dependent claim 2 are disclosed in the original claim 2 and on page 3, lines 10 to 13, of the original description. Claims 3 to 7, 9 to 13 and 15 to 17 mainly correspond to the original claims 3, 6, 7, 10, 4, 14, 15, 11, 12, 29, 23, 24 and 25 respectively. Claim 8 is supported by the original claims 5 and 13 and claim 14 by the original claims 19, 21 and 22.

3. None of the documents cited in the search report discloses a process comprising twice aging a silica-titania cogel hydrogel under the conditions stated in claim 1. Therefore, the claimed process is new over the cited prior art.

4. D1 represents the closest prior art. It discloses a process for preparing a silica-containing composition which is catalytically active for olefin polymerisation. This process comprises (i) adding a titanium compound to a strong acid such as sulfuric acid, (ii) introducing an alkali metal silicate into the said mixture to form a hydrogel, (iii) aging the hydrogel for a period of time greater than one hour, (iv) washing the thus aged hydrogel to produce a substantially alkali metal-free hydrogel, (v) forming a mixture comprising the washed hydrogel and an oxygen-containing, water soluble organic compound, (vi) separating the organic compound and water from the mixture to form a xerogel, and (vii) heating the xerogel also containing chromium at a temperature of 900 to 1800°F (482-982°C). The pH of the formed hydrogel is from 3 to 9, for example about 6, and the subsequent aging step is carried out at a temperature within the range of 65 to 200°F (18-93°C), for example at about 194°F (90°C) for about 4 hours. Removal of the water from the hydrogel is effected either by repeated washing with the organic compound or preferably by azeotropic distillation. The catalyst supports produced by this process have a surface area of 200- 500 m^2/g, a pore size of 200-600 D, a pore volume of 1.8 to 3.5 cm^3/g and a narrow pore size distribution (see claims 1, 8 and 10; column 2, lines 10 to 24; column 3, lines 24 to 27 and 63 to 67; example 1). The catalysts of D1 lead to high-melt index, low-density polymers (see column 1, lines 32 to 46; column 5, lines 29 to 33 and Table).

4.1. Starting from D1, the technical problem underlying the process comprising azeotrope-drying can be seen in the

provision of a process for the preparation of a porous inorganic oxide, which leads to catalyst supports and catalysts for olefin polymerisation exhibiting improved physical characteristics, in particular an increased average pore size.

It is proposed that this problem be solved by a process comprising steps (a) to (d) recited in claim 1 wherein step (d) is azeotrope-drying. This process differs from that of D1 in that two aging steps are performed at different pH values under the conditions set out in claim 1 instead of one aging step. In view of Table 4 of the description, which shows that the twice-aged, azeotrope-dried catalysts have a higher average pore radius than the once-aged, azeotropically dried catalysts, the Board is satisfied that the said problem has actually been solved by the claimed process involving azeotrope-drying.

4.2 Neither D1 nor the other documents cited in the search report and published before the priority date disclose subjecting the hydrogel to two aging steps at different pH values under the claimed conditions. None of these documents suggests that improved physical characteristics, in particular a higher average pore size, could be achieved by replacing the aging step of D1 by two aging steps under the conditions defined in claim 1. Therefore, the claimed process in the alternative involving azeotrope-drying was not obvious to the skilled person in view of the cited prior art and meets the requirement of inventive step.

5. D1 is also considered to be an appropriate starting point for the determination of the technical problem

concerning the two other alternatives of the claimed process, ie spray-drying and oven-drying.

5.1 Starting from D1, the technical problem was in this case to provide a process for the preparation of a porous inorganic oxide, which makes it possible to reduce the costs due to azeotrope-drying while obtaining satisfactory catalyst supports and catalysts for olefin polymerisation.

It is proposed that this problem be solved by a process comprising steps a) to d) recited in claim 1 wherein step (d) is oven-drying or spray-drying. This process differs from that of D1 in that the silica-titania hydrogel is subjected to two aging steps at different pH values under the conditions set out in claim 1 instead of one aging step and the azeotrope-drying is replaced by either spray-drying or oven-drying.

5.2 According to page 13 of the description, the catalysts prepared by twice aging under the claimed conditions and spray-drying have a polymerisation productivity of 2500-3500 g polymer/g catalyst.h for olefin polymerisation and exhibit a pore volume of about 1.0 cm^3/g compared to 0.8 cm^3/g for the once-aged, spray-dried material. The additional examples submitted at the appeal stage further show the positive effect of twice aging on the surface area of the catalyst and on the tear resistance and HLMI of the resulting polymers compared to a once-aged, spray-dried catalyst. Therefore, although the twice-aged, spray-dried catalyst might have physical characteristics (ie pore volume and/or average pore size) and a performance which are not as good as those of the catalysts

prepared by the process of D1, the results indicated above prove, however, that the claimed process leads to catalysts having satisfactory characteristics and performance. It is also evident that spray-drying is less expensive than azeotrope-drying. Therefore, it is credible that the problem stated above has actually been solved by the claimed process in the alternative where step (d) is spray-drying.

5.3 Regarding the alternative where the hydrogel is oven-dried, the Appellant argued that although the performance of the resulting catalyst was not as good as that of the twice-aged, spray-dried catalyst (the commercial catalyst), the twice-aged, oven-dried catalyst had, nevertheless, physical characteristics (ie pore volume, average pore size, surface area) and a performance which were also considered as satisfactory. He emphasised that a polymer productivity higher than the value indicated in Table 1 (run 105) could be obtained by optimising the operating conditions, the possible improvement being already derivable from Table 1.

Table 1 of the description shows that the twice-aged catalyst which has been dried in an oven at 150°C overnight has a higher pore volume, a higher average pore size and a lower surface area than the once-aged, oven-dried catalyst and that the pore volume and average pore size can be increased or the surface area decreased by varying the operating conditions (pH, temperature, time) of the second aging step (see runs 102 to 105). In run 105 the polymer productivity is low, however it is better than in runs 102 to 104. Tables 2 and 3 show that twice-aged catalysts which

have been oven-dried under other conditions either in the presence of a surfactant or after a washing step with n-propanol have a much higher polymer productivity, and that twice-aging increases the average pore size compared to once-aging. In view of the whole results reported in Tables 1, 2 and 3, the Board considered it plausible that the low polymer productivity obtained in run 105 can be further increased by varying the operating conditions of the second aging step and/or those of the oven drying step so as to obtain a catalyst having a satisfactory performance. It is also evident that oven-drying is less expensive than azeotrope-drying. Therefore, it is plausible, in the absence of evidence to the contrary, that the problem stated above has actually been solved by the claimed combination of twice-aging and oven-drying.

5.4 In the process according to D1, removal of water from the hydrogel is carried out by repeated washing with the water-soluble, organic compound or by azeotropic distillation so as to substantially preserve the internal pore structure and avoid collapse of the pores in subsequent steps (see column 3, lines 20 to 31, and lines 42 to 47). The azeotropic distillation in fact minimises damage to the pore structure of the silica-titania support. The skilled person would have expected that by replacing the azeotrope-drying by oven-drying or spray-drying without any further modification in the preparation method, ie without additional measures compensating at least partially for the more damaging effect of these two drying methods on the pore structure, the desired physical characteristics and performance of the olefin polymerisation catalyst would

not be achieved. The said compensating measure consists in subjecting the hydrogel to twice-aging under the claimed conditions. As already mentioned in paragraph 4.2 above, neither D1 nor the prior art cited in the search report suggests that twice-aging the silica-titania hydrogel under the claimed operating conditions and azeotrope-drying would lead to a catalyst with improved physical characteristics, in particular with an increased average pore size compared to the once-aged, azeotropically dried catalyst. Therefore, in the absence of any suggestion as to the claimed double aging and its unexpected positive effect on the pore structure in the cited documents, it was not obvious to the skilled person to subject the hydrogel to the claimed second aging step and to replace azeotrope-drying by spray-drying or oven-drying, which are less expensive but more damaging to the pore structure, in order to solve the technical problem stated above.

6. It follows from the above that the process of claim 1 meets the requirements of inventive step set out in Articles 52(1) and 56 EPC.

7. Claim 1 being allowable, the same applies to dependent claims 2 to 17 whose patentability is supported by that of claim 1.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The case is remitted to the first instance with the order to grant a patent with claims 1 to 17 submitted during the oral proceedings and a description to be adapted.

The Registrar: The Chairman:

E. Görgmaier P. A. M. Lançon