Datasheet for the decision
of 30 June 2009

Case Number: T 1414/04 - 3.3.07
Application Number: 96110293.6
Publication Number: 0750942
IPC: B01J 35/02
Language of the proceedings: EN
Title of invention:
Particulate catalyst for use in a fluidized bed
Patentee:
MITSUBISHI RAYON CO., LTD.
Opponent:
Asahi Kasei Kogyo Kabushiki Kaisha
Headword:
-
Relevant legal provisions:
EPC Art. 123(2)
Relevant legal provisions (EPC 1973):
EPC Art. 54
Keyword:
"Novelty - no (main request and auxiliary requests I to IV)"
"Late filed request not admitted - (auxiliary request V)"
Decisions cited:
-
Catchword:
-
Case Number: T 1414/04 - 3.3.07

DECISION
of the Technical Board of Appeal 3.3.07
of 30 June 2009

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Decision under appeal:  Decision of the Opposition Division of the European Patent Office posted 4 November 2004 revoking European patent No. 0750942 pursuant to Article 102(1) EPC.

Composition of the Board:
Chairman:  S. Perryman
Members:  B. ter Laan
D. Semino
Summary of Facts and Submissions

I. The appeal by the patent proprietors lies against the decision of the opposition division posted on 4 November 2004 to revoke European patent No. 0 750 942, based on European application No. 96 110 293.6. The patent was granted on the basis of three claims, the only independent claim reading:

"1. The fluidized bed process for oxidation of an olefin for producing a corresponding aldehyde or carboxylic acid; oxidation of an aldehyde for producing a corresponding carboxylic acid; oxidation of an olefin, an alcohol or an alkylaromatic hydrocarbon compound in the presence of ammonia for producing a corresponding nitrile; or oxidation of methanol in the presence of ammonia for producing hydrogen cyanide, wherein

   a particulate catalyst is selected which comprises catalyst particles of distinctive properties of 90% or more of the catalyst particles being in the range of 5 to 500 µm, on the weight-based particle size distribution and 90% or more of the 20 to 75 µm particles having a crushing strength in terms of breaking load which satisfies the following equation:

   \[ CS > A.d^\alpha \]

   wherein CS represents a crushing strength in terms of a breaking load [g-weight/particle];

   A represents a constant 0.001;

   d represents a particle diameter [µm]; and

   \( \alpha \) represents a constant 2,

   wherein the catalyst is the one indicated by either one of the empirical formulae of:
Empirical formula (1): $\text{Sb}_{10}A_{a}B_{b}C_{c}O_{x}$ (atomic ratio)

wherein

A is at least one element selected from the group consisting of Fe, Co, Ni, Mn, U, Ce, Sn and Cu, preferably at least one element selected from the group consisting of Fe, U, Sn and Cu;

B is at least one element selected from the group consisting of V, Mo and W;

C is at least one element selected from the group consisting of Mg, Ca, Sr, Ba, La, Ti, Zr, Nb, Ta, Cr, Re, Ru, Os, Rh, Ir, Pd, Pt, Ag, Zn, Cd, B, Al, Ga, In, Tl, Ge, Pb, P, As, Bi, Se and Te, preferably at least one element selected from the group consisting of Mg, La, Nb, Ag, Zn, B, Pb, P, Bi and Te;

$\ a \ is \ 1 \ to \ 10;$

$\ b \ is \ 0 \ to \ 5;$

$\ c \ is \ 0 \ to \ 10;$

Empirical formula (2): $\text{Mo}_{10}D_{d}E_{e}F_{f}O_{x}$ (atomic ratio)

wherein

D is at least one element selected from the group consisting of Fe, Ni, Co, Mn, Cr, Mg, Ca, Cu, Zn, La, Ce, Al and Sn, preferably at least one element selected from the group consisting of Fe, Ni, Co, Mn, Cr, Mg and Ce;

E is at least one element selected from the group consisting of Sb, Bi, As, P, B, Te, W and V;

F is at least one element selected from the group consisting of Li, Na, K, Rb and Cs;

$\ d \ is \ 0 \ to \ 10;$

$\ e \ is \ 0 \ to \ 10;$

$\ f \ is \ 0 \ to \ 3;$

and

Empirical formula (3): $\text{V}_{10}G_{g}H_{h}O_{x}$ (atomic ratio)

wherein G is at least one element selected from the group consisting of Li, Na, K, Rb, Cs, Tl, Mg, Ca, Sr
and Ba, preferably at least one element selected from the group consisting of K, Rb, Cs and Mg;

H is at least one element selected from the group consisting of La, Ce, Ti, Zr, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rb, Ir, Ni, Pd, Pt, Cu, Ag, Zn, Cd, B, Al, Ga, In, Ge, Sn, Pb, P, As, Sb, Bi, S, Se and Te, preferably at least one element selected from the group consisting of La, Ce, Nb, Cr, Mo, W, Mn, Fe, Co, Ni, P, Sb, Bi and Te;

g is 0 to 5; and

h is 0 to 15;

wherein in the formulae (1) to (3), O indicates an oxygen atom, and x indicates the number of the oxygen atom in the oxide formed by the elements concerned."

II. A notice of opposition against the patent was filed on 12 September 2002, in which the revocation of the patent in its entirety was requested on the grounds of, amongst others, Article 100(a) EPC (lack of novelty as well as lack of an inventive step).

The opposition was inter alia supported by
D1: Japanese patent application specification no. Hei 8-141401,
D1a: English translation of D1 and
D9: Catalogue "Micro Compression Testing Machine MCTM/MCTE" manufacturer's brochure by Shimadzu Corporation, Japan,

III. In the appealed decision, the opposition division held that the invention had been sufficiently disclosed in view of the information contained in the description regarding how to determine the crushing strength (CS).
As to novelty, D1, which was a prior art document according to Article 54(2) EPC - due to the fact that the earliest priority claim of the patent in suit was not valid -, as well as D4 and D5 differed from the present claim in the requirement for CS. Although the opponents had provided experiments according to the examples and comparative examples of D1, it was not clear how the resulting values for CS had been obtained, in particular regarding the samples that had been used. As to the catalysts according to D4 and D5, the results of the opponents' experiments contradicted those of the experiments submitted by the proprietor, apparently due to the different sources of the carrier used in the preparation of the catalysts. Therefore, it was not proven that the skilled person following the details of the relevant examples of D1, D4 and D5 would necessarily have arrived at a catalyst with the required CS, so that that feature could not be considered to be unambiguously disclosed in any of those documents and novelty could be accepted.

As regards inventive step, the crushing strength CS used in the claim corresponded to the fracture load $P$ for failure of brittle particles of diameter $d$ appearing in the conventionally used Hiramatsu formula for the tensile strength ($St$) at failure of such particles $\frac{St=2.8P}{\pi.d^2}$.

The problem to be solved was to reduce the loss of catalyst in a fluidized bed process. The solution offered, i.e. to increase the CS of particles in the range of 20 to 75 µm, was based on the finding by the
patent proprietors that for that size range CS rather than the usual attrition resistance played a role and that a comparative catalyst having a lower CS had a higher loss of catalyst. However, there was no evidence that the catalyst loss was mainly due to the loss of smaller particles. The prior art showed that 20 to 75 µm was a range typical for fluidized bed catalysts so that that range did not represent smaller particles. Therefore, most of the catalyst particles would fall within that range and it was obvious for the skilled person to seek to improve the properties of those particles. Furthermore, there were not enough examples in the patent in suit to arrive at reliable conclusions regarding the reduction of catalyst loss and from the prior art better results were known than now achieved. It was also noted that the CS requirement was only a rigorous criterion for the bigger particles in the claimed range, whereas the CS requirement was particularly undemanding for the smaller particles which could still be rather weak. From D1 the importance of having strong particles was known so that in preparing catalysts according to that teaching the skilled person would seek to prepare particles of good strength and he possessed the competence to obtain catalysts having the properties specified in the patent in suit. Therefore, the subject-matter of claim 1 lacked an inventive step.

IV. On 15 December 2004 the patent proprietors (appellants) lodged an appeal against the above decision. The prescribed fee was paid on the same day. With the statement setting out the grounds of appeal filed on 14 March 2005, further experimental evidence was submitted. By letter of 30 October 2006 additional
comments and experiments were submitted as well as four sets of three claims each as Auxiliary Requests I to IV. Auxiliary Request I referred to the ammoxidation of an olefin, an alcohol or an alkyl aromatic hydrocarbon compound. Auxiliary Request II was directed to the ammoxidation of propylene for producing acrylonitrile, Auxiliary Request III to the ammoxidation of an olefin for producing a corresponding nitrile in the presence of a catalyst of empirical formula (1) or (2) and Auxiliary Request IV to the ammoxidation of propylene for producing acrylonitrile in the presence of a catalyst of empirical formula (1) or (2).

In response to a communication by the Board dated 30 April 2009, in preparation for oral proceedings, the patent proprietors submitted additional comments by letter dated 8 June 2009.

V. By letter dated 14 November 2005 the opponents (respondents) filed comments on the grounds for the appeal together with 18 further documents amongst which were declarations and experimental reports. By letter dated 23 November 2005 additional information was submitted. By letter dated 21 December 2007 the respondents filed further comments as well as a further document. With a letter dated 18 March 2008 three additional documents were filed. In reaction to the communication sent by the Board in preparation of oral proceedings, a complete translation of D9 (D9b) and further comments were submitted with letter of 5 June 2009.
VI. Oral proceedings before the Board were held on 30 June 2009. After some exchange of arguments, the appellants submitted a further Auxiliary Request V, which is the same as the main request with the additional requirement in claim 1 that 10 to 40 % by weight of the particles should have a particle size of 44 μm or less.

VII. The appellants' arguments can be summarised as follows:

(a) The meaning of crushing strength (CS) used in the patent in suit was the load on a particle at which it broke, as measured with a Micro Compression Testing Machine manufactured by Shimadzu. CS was identical to the breaking load P, which was what the machine measured directly. That load could then be used for further calculations, such as that of the tensile strength according to the Hiramatsu formula \[ \text{St}=\frac{2.8P}{\pi d^2} \]
to which the machine brochure D9 or its translations D9a and D9b referred.

(b) The invention lay in the recognition that the CS of a specified part of the catalyst particles should have a minimum value. Once the skilled person knew that value, he was capable of preparing a catalyst fulfilling the requirements. That was illustrated by the respondents who had shown that a skilled person was capable of preparing at will a catalyst falling within or outside of the claimed requirements.
(c) D1 disclosed a catalyst having particles with an average size of from 20 to 100 µm and a crushing strength of 34 MPa or more. The crushing strength of D1 was however not the same as the CS according to the patent in suit. D1 mentioned the use of a Micro Compression Testing Machine to measure the crushing strength, but it was not clear how the direct measurement of that machine, i.e. the breaking load, was used to obtain the crushing strength as the Hiramatsu formula was not mentioned. From D9, in which the formula was mentioned without any context, it could not be concluded that it was always used to process the data actually measured. Many other formulae could be used to that end.

Furthermore, in order to calculate the St of the Hiramatsu formula from the breaking load, the diameter of the measured particle should also be known. The machine could not measure the diameter, so that it was not likely that the St was automatically calculated by the machine, using that formula.

Therefore, the Hiramatsu formula could not be applied to interpret the information of D1, so that it was not correct to calculate the breaking load from the crushing strength given in D1 by using that formula.

Finally, doubts were expressed as to whether the machine was at all suitable for the measurement of the present small particles.
(d) D1 disclosed that the particles should have an average size of from 20 to 100 µm, but it did not describe the importance of the range of 20 to 75 µm of present claim 1. Nor did it indicate the necessity of at least 90% of those particles having the minimum CS. In view of the scattering of the crushing strength values it was necessary to indicate the meaning of values in statistical terms. D1 did not disclose which percentage of the particles should have the required strength. If the particles on average fulfilled the crushing strength requirement of D1, some very strong bigger particles and some very weak smaller particles could be present. Therefore, D1 did not clearly and unambiguously disclose the CS of present claim 1.

(e) Regarding the auxiliary requests, the claims 1 according to those were more restricted than claim 1 as granted and referred to specific reactions not disclosed in D1. In particular, the reference in D1 (paragraph [0019]) to the reaction of alkenes was made only in the context of the reaction of impurities present in alkanes and was therefore of no relevance. Auxiliary Request V contained an additional limitation regarding the particle size which rendered the claimed subject-matter novel.
VIII. The arguments of the respondents can be summarized as follows:

(a) The respondents agreed with the interpretation of the meaning of CS given by the appellants.

(b) In D1 (D1a), the machine used for measuring the crushing strength was identified as an MCTM-500. That machine was described in D9 (D9a, D9b), a brochure of its manufacturer Shimadzu. D1 expressed the crushing strength as MPa, which was the dimension of the tensile strength (St) obtained by the machine by using the Hiramatsu formula mentioned in D9b. Therefore, it was clear that that formula had been used in D1. Moreover, D9b also described the presence of a microscope, hence the means to measure the diameter of the particle to be tested and it also indicated that the particles could have a diameter of 1 to 500μm. In fact, when one bought and used the MCTM, one had no choice but to use the Hiramatsu formula. Therefore, it was permissible to use the Hiramatsu formula for calculating the breaking load out of the crushing strength given in D1.

(c) D1 disclosed particles with an average size of 20 to 100 μm and a minimum crushing strength of 34 MPa. Applying the Hiramatsu formula, that resulted in a breaking load P of 9.7 g for a particle having a diameter of 50μm, i.e. almost four times that of the CS of present claim 1, which according to the patent in suit should be at least 2.5 g for such a particle. D1 disclosed particles in the same range as in present claim 1 and even taking
into account some scattering of the values, if one prepared particles with a diameter of 50 µm having the required minimum crushing strength according to D1, all particles had a CS above the required minimum value now being claimed. That was illustrated in Declaration No. 4 of Mr. Hideo Midorikawa, Figure C, submitted by letter of 14 April 2004 (D15). In D1 the catalyst was used for the ammoxidation of various hydrocarbons for the production of nitriles. Hence, D1 disclosed all the features of granted claim 1, which therefore lacked novelty.

(d) The subject-matter of Auxiliary Requests I to IV was not novel for the same reasons as the main request.

(e) Auxiliary Request V was late filed and it did not comply with the requirements of Article 123(2) as the additional requirement had originally been described as belonging to the prior art, not to the invention.

IX. The appellants (patent proprietors) requested that the decision under appeal be set aside and the patent be maintained as main request as granted or auxiliarily on the basis of Auxiliary Requests I to IV filed 30 October 2006 or of Auxiliary Request V filed at the oral proceedings on 30 June 2009.

The respondents (opponents) requested that the appeal be dismissed.
Reasons for the Decision

1. The appeal is admissible.

Novelty

2. D1 (D1a) discloses a catalyst for producing a nitrile by a catalytic oxidation reaction of a hydrocarbon with ammonia in the gaseous phase, the catalyst being a composite oxide produced by subjecting to heat treatment a dried product obtained by spray-drying a solution or slurry containing silica, molybdenum and/or vanadium, the catalyst having a silica content of from 40 to 70 % by weight, an average particle size of from 20 to 100 µm, a crushing strength of 34 MPa or more and a bulk density of up to 1.2 g/cm³ or less (claim 1).

The crushing strength is measured by means of a Micro Compression Testing Machine (paragraph [0015], page 12 of D1a), in particular a MCTM-500; manufactured and sold by Shimadzu Corporation (paragraph [0028], page 19 of D1a).

2.1 D9 (D9b) is a brochure from the manufacturer of that machine, Shimadzu. It carries no date, but it was not contested that the machine was on the market before the priority date of the patent in suit. Therefore, D9b can be accepted as prior art.

D9b describes, under the heading "Measurement Principle", how the test force is applied to the specimen, allowing dynamic measurement of the deformation characteristics of fine particles. Specimen size can be measured using a microscope. The specimen's
mechanical strength (tensile strength) is determined from the load causing it to break. It is possible to individually compress particles from 1 to 500 µm in diameter. Finally, D9b says that the mechanical strength of particles is acquired using the equation of Hiramatsu et al.  

\[
St = \frac{2.8P}{\pi d^2}
\]

St: tensile strength (kgf/mm² or N/mm²)  
P: load (kg or N)  
d: particle diameter (mm),  

referring to the article of Hiramatsu, Oka, Kiyama: Journal of the Japanese Mining Association, 81 10.24 (1965) (D26). On page 14 of D9b, specifications of various machines, amongst which the MCTM-500, are given. All of them include an "Optical monitor" under which the total magnification and the objective lens are indicated, as well as an "Optical head", under which the effective measurement range is mentioned. The MTCM series is indicated as "Display measurement type", the MCTE as "Microscopic measurement type". On the picture of the MCTM on page 14, a microscope is visible as part of the set-up.

Therefore, from D9 it can be seen that means to measure the diameter of the particles to be compressed are part of the MCTM and also that the Hiramatsu formula is automatically applied when using the machine, in order to calculate the mechanical strength or tensile strength of the particle. Furthermore, the use of the MTCM-500 is explicitly described in D1 for measuring the crushing strength, and the dimension of the tensile or mechanical strength of D9b (kgf/mm² or N/mm²) and the crushing strength of D1 (MPa; Pa=N/mm²) correspond. In addition, although the appellants had argued that many
other formulae could be used in order to calculate the crushing strength from the breaking load, no such other formula had been indicated in a more specific way, nor had any evidence of the existence of such alternatives been given. In view of all this, the application of the Hiramatsu formula to the crushing strength given in D1 in order to calculate the breaking load, is fully justified.

2.2 Claim 1 of the patent in suit requires that in the claimed process

- 90% or more of the catalyst particles should be in the range of 5 to 500 µm, on the weight-based particle size distribution, and

- 90% or more of the 20 to 75 µm particles should have a crushing strength greater than 0.001 d².

2.2.1 According to D1, the catalyst particles should have an average particle size of from 20 to 100 µm. In the experiments provided by both parties relating to catalysts according to D1, more than 99.99% of the catalyst particles were in the range of 5 to 500 µm. Therefore, even taking into account the usual scattering of particle sizes around the average value, the first requirement can be considered to be fulfilled by D1. That was not contested.

2.2.2 Regarding the second requirement, according to D1 the catalyst should have a crushing strength of 34 MPa or more. It was uncontested that that, applying the Hiramatsu formula to particles having a diameter of 50 µm, corresponded to a breaking load of 9.7 g/particle or more, whereas according to present claim 1 the CS value for such a particle was required to be above 2.5
g/particle. In fact, over the whole range of particles with a diameter of from 20 to 100 µm, the minimum requirement for the breaking load - calculated by application of the Hiramatsu formula to the crushing strength according to D1 - is almost four times the minimum requirement for the CS according to the patent in suit. Therefore, that is also valid for the range of 20 to 75 µm particles.

The requirement of D1 that "the catalyst" should have a crushing strength of 34 MPa or more, means on a literal interpretation that all the catalyst particles should have that strength, so that also the second requirement according to the patent in suit would be fulfilled. Even if one would interpret the strength requirement of D1 as an average for the total of the particles, a factor four between the minimum breaking load calculated from D1 and that according to the patent in suit is sufficient for at least 90% of the particles to have the strength now being required. All the more so since the number of particles actually measured according to the patent in suit, is limited (100; paragraph [0075]) compared to the total of the catalyst particles, so that a great error margin is present. That is confirmed by the experimental evidence filed by both parties, from which it can be seen that hardly any particles have a smaller crushing strength than one fourth of the average value of all particles.

This is in particular supported by Declaration No. 4 of Mr. Midorikawa, filed with letter of 14 April 2004 (D15), where the preparation of a catalyst according to Example 2 of D1 is described. That declaration is of course no prior art by itself, but it shows which
properties were present in the catalysts of D1, which is prior art. Declaration No. 4 can therefore be accepted into the proceedings. Fifty of the particles so prepared were tested on their crushing strength. In Figure C it can be seen that about 90% of the particles fulfilled the strength requirement of D1, whereas all particles fulfilled the CS-requirement of the patent in suit. Counter experiments by the Appellants (filed with letter dated 30 October 2006) showing that catalyst particles did not necessarily have the necessary CS, showed at the same time that those particles that fulfilled the strength requirement of D1, also fulfilled the CS-requirement of the patent in suit (Figures 1 to 4). Also, those particles that did not fulfil the present CS requirement, did not fall under the requirements of D1 either, so that it cannot be said that they had been prepared according to Example 2 of D1, which explicitly requires a minimum crushing strength of 34 MPa.

In view of the above, one cannot but arrive at the conclusion that the skilled person, when preparing a catalyst that fulfils the requirements set out in D1, inevitably arrives at a catalyst that complies with the requirements for the catalyst particles in claim 1 of the main request.

2.3 Furthermore, the catalyst of D1 which comprises an oxide containing molybdenum and/or vanadium (paragraph [0007]) falls under one or both of the empirical formulae (2) and (3) of claim 1 of the present main request and it is used in the catalytic oxidation of hydrocarbons in the gaseous phase in the presence of ammonia for producing a nitrile (paragraph [0019]).
Therefore, the additional features of the claimed process of the main request related to the catalyst composition and type of process, are also known from D1, which was not contested.

2.4 In view of the above, the process claimed according to claim 1 of the main request is not novel.

Auxiliary requests

3. Claim 1 of Auxiliary Request I has been restricted to the ammoxidation of an olefin, an alcohol or an alkyl aromatic hydrocarbon compound. Claim 1 of Auxiliary Request II was restricted to the ammoxidation of propylene for producing acrylonitrile, claim 1 of Auxiliary Request III to the ammoxidation of an olefin for producing a corresponding nitrile in the presence of a catalyst of empirical formula (1) or (2) and claim 1 of Auxiliary Request IV to the ammoxidation of propylene for producing acrylonitrile in the presence of a catalyst of empirical formula (1) or (2).

3.1 Those ammoxidation reactions are, however, also disclosed in D1, paragraph [0019], where the ammoxidation of hydrocarbons is described and where it is said that: "Examples of hydrocarbons include alkanes and alkenes, .... " and " .... the catalyst of the present invention can also be used for producing a nitrile by subjecting an alkene, such as propylene or iso-butene, to a catalytic oxidation reaction with ammonia in the gaseous phase." Therefore, reading the whole of that paragraph reveals that the ammoxidation of alkenes is not only mentioned in the context of
impurities in the alkane feedstock, so that the appellants' argument in that sense cannot be followed.

3.2 As the restrictions incorporated into the subject-matter of claim 1 of Auxiliary Requests I to IV do not add any distinguishing feature over D1, the reasons regarding the main request are equally valid so that the processes claimed in those Auxiliary Requests are not novel either.

4. Auxiliary Request V was submitted at a very advanced stage of the proceedings. Its claim 1 contains a restriction regarding the particle size, requiring that 10 to 40 % by weight of the particles should have a particle size of 44 µm or less, which feature is taken from paragraph [0010] of the patent specification (corresponding to page 3, lines 20 to 33, in particular lines 28 to 29, of the original application). As that passage however refers to the state of the art, it is doubtful whether features of it can be seen as belonging to the invention. Moreover, further features mentioned in that passage have not been incorporated in the claim, so that the question arises whether the singling out of features is allowable. Therefore, claim 1 of Auxiliary Request V is not clearly allowable. Moreover, incorporating a feature from the description at such a late stage of the proceedings without any new objection having been raised, might lead to a fresh case and hence its admission into the proceedings would contravene Article 13(3) of the Rules of Procedure Boards of Appeal (OJ 2007, 536). For those reasons, Auxiliary Request V cannot be admitted into the proceedings.
Order

For these reasons it is decided that:

The appeal is dismissed.

Registrar

Chairman

S. Fabiani

S. Perryman