BESCHWERDEKAMMERN DES EUROPÄISCHEN PATENTAMTS | BOARDS OF APPEAL OF THE EUROPEAN PATENT OFFICE | CHAMBRES DE RECOURS DE L'OFFICE EUROPEEN DES BREVETS

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File Number: T 134/90 - 3.3.3

Application No.: 79 301 996.9

Publication No.: 0 011 914

Title of invention: Titanium trichloride catalyst composition and its use in the polymerization of alpha-olefins

Classification: C08F 10/00

D E C I S I O N
of 18 October 1991

Proprietor of the patent: EXXON RESEARCH AND ENGINEERING COMPANY

Opponent: SOLVAY

Headword:

EPC Article 56

Keyword: "Inventive step (no) - prior art documents pointing at the claimed solution - no unexpected effects"

Headnote

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Beschwerdekammern | Boards of Appeal | Chambres de recours

Case Number : T 134/90 - 3.3.3

D E C I S I O N
of the Technical Board of Appeal 3.3.3
of 18 October 1991

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Decision under appeal : Decision of Opposition Division of the European Patent Office dated 25 October 1989, posted on 22 December 1989 rejecting the opposition filed against European patent No. 0 011 914 pursuant to Article 102(2) EPC.

Composition of the Board :

Chairman : C. Gérardin
Members : R. Lunzer
R. Schulte

Summary of facts and submissions

I. The mention of the grant of the patent No. 0 011 914 in respect of the European patent application No. 79 301 996.9 filed on 25 September 1979 and claiming priority of 26 September 1978 of an earlier application in the United States, was published on 5 March 1986 on the basis of 21 claims.

Claim 1 reads as follows:

"A substantially non-friable, highly active Ziegler-type TiC_{13} catalyst composition for use with an organoaluminum compound in the polymerization of alpha-olefins which is prepared by the following sequence of steps:

(1) contacting $TiCl_4$ with an organoaluminum compound at a temperature in the range of -50°C to 30°C to produce a $TiCl_3$ reduced solid product,

(2) contacting the reduced solid product with an α-olefin having from 3 to 8 carbon atoms under polymerization conditions to obtain a $TiCl_3$ reduced solid product containing from 3 to 100 wt.% of prepolymerized α-olefin based on the weight of $TiCl_3$, and

(3) treating the prepolymerized reduced solid with at least one of (a) a chlorinated hydrocarbon having at least 2 carbon atoms and a Lewis base complexing agent or (b) $TiCl_4$ and a Lewis base complexing agent to convert the prepolymerized $TiCl_3$ reduced solid to a substantially non-friable highly active, crystalline $TiCl_3$ composition."

Claims 2 to 20 are dependent claims directed to preferred embodiments of the subject-matter of the main claim.

Further, Claim 21 concerns a process for the polymerisation of alpha-olefins in the presence of a catalyst component according to any of Claims 1 to 20 and an organoaluminium compound as cocatalyst.

II. On 29 November 1986 the Opponent filed a Notice of Opposition against the grant of the patent on the grounds that the requirements of Article 52(1) EPC, i.e. Articles 54(2) and 56 EPC, were not met (Article 100(a) EPC). The arguments which were presented i the Statement of Grounds of Opposition filed simultaneously as well as subsequently in the course of the opposition procedure, however, concerned only an objection of lack of inventive step with regard to the teaching of mainly the following documents:

(1) GB-A-1 391 068
(2) US-A-3 442 820
(3) BE-A-844 951.

III. By a decision delivered orally on 25 October 1989, with written reasons posted on 22 December 1989, the Opposition Division rejected the opposition. It was first stated in that decision that none of the documents (1) to (3) described a crystalline titanium trichloride catalyst component prepared from titanium tetrachloride by a process comprising a reduction step, a prepolymerisation step and an activation step as specified in Claim 1 of the patent in suit, and that, consequently, the requirement of novelty was met. Further, an inventive step was involved as well, since document (1), which related to the preparation of the delta form of titanium trichloride, did not suggest the prepolymerisation step. Although such treatment was known from document (2) to produce less friable catalyst particles, that teaching could not lead

to the claimed subject-matter for two reasons: the first one was that it was strictly limited to the polymerisation of ethylene; the second one was that document (2) said nothing about a possible subsequent activation step. Nor was the teaching of document (3) relevant, since it was primarily concerned with the preparation of an activated catalyst in the beta form.

IV. The Appellant (Opponent) thereafter lodged a Notice of Appeal on 20 April 1990 and paid the prescribed fee at the same time. The arguments presented in the Statement of Grounds of Appeal filed simultaneously, in a further written submission and at oral proceedings held on 18 October 1991 were confined to the issue of inventive step.
The reduced friability of catalyst particles mentioned in document (2) as the result of ethylene prepolymerisation was exactly the effect obtained with an α-olefin having 3 to 8 carbon atoms in the patent in suit. The treatment with propylene mentioned in document (3) occurred on a reduced solid before the treatment with an ether, and resulted in improved granularity of the catalyst particles; the comparison between Examples 1 and 7 showed that only the specific area and the porosity were affected by propylene prepolymerisation, but that the general properties of the catalyst remained substantially the same. There was thus no prejudice to be overcome against including a prepolymerisation step between the reduction step and the activation step as described in document (1).

In the Statement of the Grounds of Appeal, more specifically, the Appellant relied on several additional documents, in particular on the translation in English of JP-A-142 691/77 (document (7)), which had been considered in the examination procedure in the form of a summary

published in Chemical Abstracts, 1978, Volume 88, 121,933 g. That citation described a three step process for the preparation of activated titanium trichloride, wherein prepolymerisation could take place after the reduction step; according to Example 3, the activation step comprised a treatment with an ether and with titanium tetrachloride.

V. The arguments presented by the Respondent (Patentee) in the Counterstatement filed on 9 November 1990, and in later submissions, as well as during oral proceedings can be summarised as follows:

Document (1) stressed at length the importance of having the catalyst in a highly porous form; this could not be an incentive to apply a polyethylene coating in accordance with the teaching of document (2). Regarding the nature of the polyolefin, the skilled man would be aware of the difference between ethylene and propylene, since the former polymerised vary fast to give rise to a true polyethylene coating, whereas the latter polymerised more slowly, resulting in a polymer which penetrated and encapsulated the catalyst particles. The essence of document (3) was to produce a special form of titanium trichloride and the prepolymerisation step should be interpreted in that context; further, the reference to granularity could not be restricted solely to particle size, but comprised a wide range of particle parameters.

As far as document (7) was concerned, Example 3 showed that the maximum amount of propylene which could possibly be polymerised onto the catalyst species was 0.35 weight percent based on the weight of titanium trichloride, which was well below the minimum level of 3 weight percent required in the patent in suit.

VI. 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.

Reasons for the Decision

1. The appeal complies with Articles 106 to 108 and Rule 64 EPC and is admissible.

2. As it appears from paragraph IV above, the Appellant relied partly on several new documents to substantiate its appeal. After examination of these citations, the Board found document (7) more relevant than any of the documents previously submitted, since it describes the preparation of activated titanium trichloride by a three step process comprising (i) the reduction of titanium tetrachloride with an organoaluminium compound, (ii) the prepolymerisation of propylene, which can be carried out before, during or after the former reaction, the amount of propylene being preferably 0.001 to 1, especially 0.01 to 0.1, based on the total amount of titanium tetrachloride, and (iii) the treatment with a Lewis acid and/or a complexing agent (Claims 1, 2 and 6; page 7, lines 17 to 19). According to Example 3, to which the Appellant referred more specifically, the final activation (iii) comprises a treatment with diisoamyl ether and titanium tetrachloride, but the amount of propylene which is polymerised onto the catalyst species is only 0.35 weight percent, based on the weight of titanium trichloride (Counterstatement of Appeal, points (C4) and (C5)). This means that, although there is no specific combination of features in document (7) falling within the terms of Claim 1 of the patent in suit, this citation discloses the claimed subject-matter in general terms.

In his introductory statement in the oral proceedings, accordingly, the Chairman informed the parties that the Board, in exercising its discretionary power, had decided to admit document (7) into the proceedings (Article 114(1) EPC). The Appellant, however, took the view that the documents (1) to (3) were sufficiently relevant by themselves to demonstrate that the claimed subject-matter did not involve an inventive step and that, consequently, he would not rely on document (7). Although, in the Board's opinion, an argument based on the teaching of that citation would have been even stronger, it would not have led to any different ultimate outcome for the reasons which appear below. Therefore, the Board decided to follow the line adopted by the Appellant; there will thus be no further reference to document (7).

3. The patent in suit concerns a titanium trichloride catalyst composition of the delta type and its use in the polymerisation of alpha-olefins. Such a titanium trichloride catalyst composition is described in document (1) which the Board regards as the closest state of the art. That citation describes a process for the preparation of a solid catalytic complex of titanium trichloride, in which titanium tetrachloride is reduced by an organoaluminium compound, (b) the reduced solid thus obtained is treated with a complexing agent containing one or more electron donor atoms, and (c) either after step (b) or simultaneously therewith the said solid is reacted with titanium tetrachloride (Claims 1, 2 and 5 in combination with page 2, column 1, line 50 to column 2, line 2). This dual treatment results in the change of the crystalline structure of titanium trichloride from the beta form into the delta form (page 3, lines 27 to 28; page 4, lines 115 to 121; page 9, lines 30 to 33). In

combination with a cocatalyst, especially an organoaluminium compound identical with the reducing agent used in step (a), these catalytic complexes permit very high stereospecificity and activity to be attained (page 5, lines 74 to 94; page 6, lines 92 to 102 and 117 to 122). However, when subjected to mechanical shearing forces which may occur during the activation step and/or subsequently during the polymerisation reaction, these catalytic complexes have a tendency to shear into smaller particles, or fines, which has a direct impact on the granularity of the polymer particles, since the latter are essentially replicates of the former.

In the light of this shortcoming the technical problem underlying the patent in suit can thus be seen in reducing the friability of the catalytic complexes without substantially affecting the above-mentioned advantageous properties, i.e. without reducing the stereospecificity and yield to unacceptable levels.

This problem is solved according to Claim 1 of the patent in suit by carrying out, between the reducing step (a) and the complexing/activating steps (b)/(c), a prepolymerisation step with an alpha-olefin having 3 to 8 carbon atoms so as to obtain a titanium trichloride reduced solid product containing from 3 to 100 weight percent of prepolymerised alpha-olefin based on the weight of titanium trichloride.

In view of the experimental data in Table III of the patent in suit, which show the influence of the prepolymerisation step on the presence of catalyst fines, on the catalyst efficiency and on the proportion of amorphous polypropylene for a given catalyst system, the Board is satisfied that the above-defined technical

problem has been effectively solved. These results have not been disputed by the Appellant.

4. After examination of the documents relied upon by the Appellant the Board has come to the conclusion that this technical teaching is not disclosed in any of them and that the subject-matter of the patent in suit is, therefore, novel. Since the issue of novelty is no longer raised by the Appellant, it is not necessary to consider this matter in detail.

5. It still remains to be examined whether the subject-matter of the patent in suit as defined in Claim 1 involves an inventive step with regard to the teaching of documents (1) to (3).

5.1 Document (3) concerns the preparation of catalyst components, which are suitable for the polymerisation of olefins, by a sequence of operations comprising (i) the reduction of titanium tetrachloride with an organoaluminium compound, (ii) optionally a heat treatment of the reduced product, (iii) the treatment with an ether or polyether at a temperature between 70 and 120°C, and (iv) a washing step of the final product with an inert hydrocarbon solvent (Claim 9). According to a preferred embodiment, that process comprises an additional intermediate operation carried out before step (iii), which consists in the addition of a small amount of an alkylaluminium compound, followed by the introduction of 0.2 to 1 gram of propylene or another olefin per gram of catalyst, whereby polymerisation of that monomer occurs; that prepolymerisation step is said to improve the "granularity" and the apparent density of the polymer (page 5, lines 7 to 15; Example 7). In combination with organoaluminium compounds, these catalyst components, wherein titanium trichloride is in the beta crystalline

form, display both high activity and stereospecificity (page 2, line 38 to page 3, line 24; page 7, lines 12 to 30).

5.2 Without disputing that analysis the Respondent argued that the sole reference to improved granularity could not be equated with the beneficial effect on friability achieved in the patent in suit, and that, consequently, the teaching of document (3) could not lead to the claimed subject-matter. That argument cannot be accepted for the following reasons:

5.2.1 In the first place, it seems appropriate to make clear what is actually meant by improved" granularity". According to Encyclopaedia Universalis, Volume 7, page 949, 1980, published by Encyclopaedia Universalis France, Paris, as well as Grand Larousse Encyclopédique, Volume 5, 1979, published by Librairie Larousse, Paris, granularity (granulométrie) refers to particle size and particle size distribution of a granular material. Neither of the definitions contains the least reference to another parameter, like porosity, as the Respondent alleged in the Counterstatement of Appeal (point (A7)).

It follows that improved granularity involves both improved particle size, which in that context would only be interpreted by the skilled man as larger catalyst particles, and improved particle size distribution, which can only mean narrower size distribution.

5.2.2 Technical evidence of the influence of an intermediate prepolymerisation step on these two parameters has been provided by the Appellant together with the reply filed on 30 August 1991.

For that purpose, the Appellant has repeated the preparation of the titanium trichloride catalyst components according to Example 1, thus without an intermediate prepolymerisation step, and according to Example 7, thus comprising such additional step, of document (3). The photomicrographs of the two catalyst components clearly show that the catalyst particles which have been subjected to prepolymerisation are generally larger and more homogeneous (Annex, Figures 1 and 2). More specifically, it appears that 77% of the catalyst particles have a diameter lower that 10 μm in absence of prepolymerisation, and that 66% of these particles have a diameter between 20 and 40 μm after such prepolymerisation (point IV).

In another experiment, the influence of prepolymerisation on the friability of the catalyst particles according to Example 7 of document (3) has been examined by subjecting these particles to shearing forces following the method described in the patent in suit, page 7, lines 15 to 17. The comparison of the photomicrograph of the catalyst particles which have been subjected to that mechanical treatment (Annex, Figure 3) with the photomicrograph of the untreated particles (Annex, Figure 2) shows that the texture of the prepolymerised reduced solid is not modified, which means that the latter is non-friable (point V, page 6, paragraphs 1 and 2).

Although this experimental evidence was submitted at a rather late stage, the Board has decided to admit it since it does not illustrate new arguments as such, but merely confirms and supports arguments previously presented in the Statement of Grounds of Appeal (page 6, last paragraph). That already was the approach followed in the unpublished decision T 324/88 of 8 February 1989, wherein the Board took the view that technical evidence filed in support of an argument previously submitted could be

accepted in spite of its lateness (Reasons for the Decision, points 6 änd 8).

5.2.3 This link between encapsulation and friability has already been mentioned in document (2), which teaches that one of the advantages obtained by encapsulating reduced titanium trichloride catalyst particles with a layer of polyethylene is the lower friability of these particles.

The authors of that citation start from the finding that in the polymerisation of olefins in the presence of a diluent and small amounts of titanium trichloride catalyst, which has been obtained by reduction of titanium tetrachloride with an organoaluminium compound, and an organoaluminium compound as cocatalyst, loosely agglomerated bridges and webs of polymer particles are formed within the polymerisation reaction vessel. That phenomenon is attributed to the fact that, in the presence of the organoaluminium activator, a relatively high proportion of the titanium trichloride cocatalyst is soluble in that hydrocarbon diluent, causing the polymer product to precipitate from solution in fibrous form. In order to overcome that difficulty, the document suggests decreasing the hydrocarbon solubility of the catalyst particles by subjecting them to a treatment with ethylene in polymerising conditions, resulting in the formation of a layer of polyethylene on the surface of these particles (column 1, line 68 to column 2, line 40 in combination with column 1, lines 26 to 29; column 3, line 75 to column 4, line 21).

In addition to that primary effect, the authors found that the surface coating causes a substantial decrease in density, lessening thus the tendency of the particles to come out of suspension, and, above all, reduces the friability of these particles, which are consequently less

subject to attrition resulting from the agitation (column 4, line 63 to column 5, line 11). It is in particular explicitly stated that the untreated particles are quite friable and tend to diminish in particle size until practically colloidal size particles remain, resulting in colloidal size polyolefin particles which are difficult to work with upon completion of the polymerisation. Further, it can be concluded that encapsulation has no major detrimental effect on the catalyst activity, since it is stated that excellent yields of polymer per unit of catalyst are achieved (column 2, lines 22 to 26).

Although the teaching of document (2) is strictly limited to the encapulation of catalyst particles with a polyethylene coating, it provides an illustration, even without the late technical evidence submitted by the Appellant, of the effects of propylene prepolymerisation on such particles mentioned in document (3), since, for the reasons which will appear below when discussing porosity, the difference between ethylene and propylene cannot be regarded as essential in the present context.

5.3 The comparison between Examples 1 and 7 of document (3) makes it possible to appreciate the influence of the additional prepolymerisation step on various catalyst parameters and properties (Statement of Grounds of Appeal, page 7, Table).

According to Example 1, thus following the general method of that citation, the reduction of titanium tetrachloride by an organoaluminium compound is followed by a heat treatment, then by a treatment with n-butylether (page 7, line 24 to page 8, line 8). According to Example 7, in contrast, the heat treatment of the reduced solid is followed by the prepolymerisation of propylene in the

presence of an organoaluminium compound; after that additional step the normal complexing with n-butylether occurs as above (page 15, lines 16 to 27). Following data are given:

	Example 1	Example 7
- specific surface area (m^2/g)	13.02	2
- porosity (cm^3/g)	0.085	0.021
- yield (g.pol/g.cat x h x P.prop)	114	110
- fraction insoluble in heptane (%)	97	96

From these figures the Appellant concludes that only the specific surface area and the porosity are substantially affected by prepolymerisation, whereas the essential properties of the catalyst, namely activity and stereospecificity, remain practically the same. The Respondent, on the contrary, argues that the two catalysts are not equivalent in their compositions, in that the catalyst subjected to prepolymerisation has higher aluminium and chlorine contents as the result of the addition of the organoaluminium compound, which has a detrimental influence on the catalyst activity (Counterstatement of Appeal, point (A9)).

In the Board's view, however, this rather speaks for the Appellant's position, because it means that the actual loss of catalyst activity due to prepolymerisation in Example 7 is even less than 3.5%. In reality, whatever the exact contribution of prepolymerisation and difference in composition to the reduction of catalyst activity, the above noted loss of 3.5% is significantly lower than in the patent in suit (page 11, Table III), from which it

appears that the prepolymerisation treatment lowers the catalyst activity by more than 18%. This means that in the patent in suit the elimination of catalyst fines can only be achieved at the cost of a non-negligible loss of catalyst activity; by the same token, this shows that there was no prejudice against an intermediate prepolymerisation step by following the teaching of document (3).

5.4 As noted above, prepolymerisation results according to document (3) in a reduction of porosity of the catalyst particles by a factor of 4. Although that may appear at first sight as a dramatic change, it should be appreciated by reference to the general teaching of that citation, that one can obtain highly active catalysts which have a low specific surface area, in practice between 1 and 50 m^2/g, corresponding thus to a ratio of 50 (page 2, line 38 to page 3, line 12; page 4, lines 10 to 14). On the other hand, document (1) indicates that catalysts which are very porous and where specific surface area extends over a wide range can be equally active; that parameter should generally be greater than 75 m^2/g, the preferred range extending up to 200 m^2/g, corresponding thus to a ratio of 2.7 (page 4, lines 25 to 70).

Both documents concur thus in showing that porosity and specific surface area can vary within wide limits and that, consequently, they are not essential parameters in the present case. This is why the teaching of document (2) would be considered by the skilled man for the solution of the problem underlying the patent in suit. The difference underlined by the Respondent (Counterstatement of Appeal, point (B2)) between ethylene used in document (2), on the one hand , and propylene used in document (3) as well as in the patent in suit, on the other hand, i.e. lower polymerisation rate of propylene resulting in a polymer

which not only encapsulates the catalyst particles as polyethylene would do, but additionally penetrates these particles, is not disputed, but it has not been made credible that it could affect to a significant extent the parameters directly responsible for catalyst activity. The fact that the teaching of document (2) is strictly limited to encapsulation with polyethylene is, therefore, a minor point for the skilled man, who would expect that the advantages there disclosed, of improved uniformity of particle size, and reduced friability, would be equally attainable if prepolymerisation were to be performed using higher olefins.

5.5 The solution claimed in the patent in suit does not lead to any surprising results with respect to both catalyst activity and stereospecificity when compared with the levels achieved for these two parameters in documents (1) and (3).

The catalyst activity is said to be somewhat greater than 2,200 grams of polymer formed per gram of titanium trichloride in the patent in suit (page 6, lines 39/40). By comparison, according to document (1) that parameter is of the order of 1,900 grams of polymer per hour per gram of titanium trichloride in the catalyst complex (page 6, lines 117 to 122).

Further, according to document (1), the proportion of amorphous polypropylene formed, i.e. the fraction soluble in hexane, is generally lower than 5% and commonly lower than 2% (page 6, lines 92 to 100; Examples). Similarly, document (3) mentions stereospecificities of 97 and 96% in Examples 1 and 7. All these data are comparable with the two figures, i.e. 97.6 and more than 95%, disclosed in the patent in suit (page 11, Table III).It follows that the solution claimed in the patent in suit does not bring other advantages than those explicitly mentioned in documents (2) and (3).

5.6 In conclusion, for the reasons given above, the subject-matter of Claim 1 does not involve an inventive step.

6. Claim 1 not being allowable, the same applies to dependent Claims 2 to 20 which are directed to preferred embodiments of the subject-matter of the main claim as well as to Claim 21, which concerns a process for the polymerisation of alpha-olefins in the presence of a catalyst component according to any of Claims 1 to 20 and an organoaluminium compound as cocatalyst, and thus all fall with it.

Order

For these reasons, it is decided that:

1. The decision under appeal is set aside.

2. The patent is revoked.

The Registrar: The Chairman:

E. Görgmaier C. Gérardin