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Aktenzeichen / Case Number / N° du recours : T 91/88 - 3.3.1

Anmeldenummer / Filing No / N° de la demande : 79 100 958.2

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Bezeichnung der Erfindung:
Title of invention:
Titre de l'invention : Process for copolymerizing ethylene

Klassifikation / Classification / Classement : C08F 210/16

ENTSCHEIDUNG / DECISION

vom / of / du 29 May 1989

Anmelder / Applicant / Demandeur :

Patentinhaber / Proprietor of the patent /
Titulaire du brevet : Union Carbide Corporation

Einsprechender / Opponent / Opposant : BASF AG

Stichwort / Headword / Référence :

EPÜ / EPC / CBE Article 56

Schlagwort / Keyword / Mot clé : "Inventive step (confirmed) - Non-obvious process feature resulting in a marked improvement of a specific property"

Leitsatz / Headnote / Sommaire

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Beschwerdekammern **Boards of Appeal** **Chambres de recours**

Case Number : T 91/88 - 3.3.1

DECISION
of the Technical Board of Appeal 3.3.1
of 29 May 1989

Appellant : (Opponent)

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Decision under appeal : Decision of the Opposition Division of the European Patent Office dated 9 November 1987, posted on 16 December 1987, rejecting the opposition filed against European patent No. 0 004 647 pursuant to Article 102(2) EPC.

Composition of the Board :

Chairman : K. Jahn
Members : C. Gérardin
C. Payraudeau

Summary of Facts and Submissions

I. The mention of the grant of the patent No. 4647 in respect to European patent application No. 79 100 958.2 filed on 30 March 1979 and claiming priorities of 31 March 1978 and 16 February 1979 from two earlier applications US 892 322 and US 12 720 was announced on 9 January 1985 on the basis of two claims.

Claim 1 reads as follows:

"A process for copolymerizing ethylene with one or more higher α-olefin monomers employing a catalyst composition prepared by forming a precursor composition from a magnesium compound, titanium compound, and electron donor compound, and then activating the precursor composition with an organoaluminium compound to form the catalyst, characterized in that the polymerization is conducted continuously in a fluid bed reactor at a temperature of 30 to 105°C under a pressure of <69 bar (<1000 psi) in the gas phase to produce ethylene copolymer containing ≥ 90 mol percent of ethylene and ≤ 10 mol percent of one or more C_3 to C_8 α-olefins at a productivity of $\geq 50{,}000$ kg of polymer per kg of Ti, said copolymer being produced in granular form and having a density of ≥ 0.91 to ≤ 0.94 g/cm^3 and a melt flow ratio of ≥ 22 to ≤ 32, by contacting the monomer charge with, in the presence of 0 to 2.0 mols of hydrogen per mol of ethylene in the gas phase reaction zone, particles of an activated precursor composition of the formula

$$Mg_mTi(OR)_nX_p[ED]_q$$

wherein R is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical, or COR' wherein R' is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical,

X is selected from the group consisting of Cl, Br, I or mixtures thereof,

ED is a liquid organic electron donor compound in which said precursor composition is soluble and which is selected from the group consisting of alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ethers, cyclic ethers and aliphatic ketones,

m is ≥ 0.5 to ≤ 56,
n is 0, 1 or 2,
p is ≥ 2 to ≤ 116, and
q is ≥ 2 to ≤ 85,

said precursor composition being impregnated in an inert porous carrier in a weight ratio of 0.033:1 to 1:1, and being activated with an activator compound having the formula

$$Al(R'')_cX'_dH_e$$

wherein X' is Cl or OR , R" and R are the same or different, and are C_1 to C_{14} saturated hydrocarbon radicals, d is 0 to 1.5, e is 1 or 0 and c+d+e=3, activation of said precursor composition being effected by treating the impregnated precursor composition outside the polymerization reactor in a hydrocarbon slurry with >0 to <10 mols of activator compound per mol of titanium compound in said precursor composition, drying the mixture to obtain a free-flowing solid particulate material, and feeding the impregnated precursor composition into the polymerization reactor wherein it is further activated by adding additional activator compound to the reactor in such amounts as to provide ≥10 to ≤400 total mols of said activator compound per mol of titanium compound in said precursor composition."

II. The Appellant (Opponent) filed an opposition against the grant of the patent on 4 October 1985 on the grounds of lack of inventive step of the two process claims with regard to the teaching of mainly the following documents:

(1) US-A-3 989 881
(2) DE-A-2 543 272
(3) DE-A-1 808 388
(4) US-A-4 003 712.

III. By a decision delivered orally on 9 November 1987 with written reasons posted on 16 December 1987 the Opposition Division rejected the opposition on the basis that the subject-matter of the patent in suit involved an inventive step. More specifically, it was held that the concept of partial activation of a catalyst precursor outside the polymerization reactor followed by complete activation inside the reactor was not taught in any cited document; furthermore, this two step treatment of the precursor composition led to a higher bulk density and a higher space time yield of the polymer, as evidenced by the additional Examples 11 and 12 filed on 13 October 1983 in examination procedure and confirmed on 28 May 1986 in opposition procedure, so that an inventive step was to be acknowledged.

IV. An appeal was lodged against this decision on 9 February 1988 with payment of the prescribed fee. A statement of grounds of appeal was filed on 11 April 1988. In these grounds the Appellant argued that the catalyst compositions were known as such from documents (1) and (2) and that the two step activation of the catalyst precursor did not give rise to the double technical effect claimed by the Respondent; although an increased bulk density could not be denied for the polymer prepared in Example 11 according to the patent in suit, this was actually achieved at the expense of a higher titanium residue in the polymer and an overall lower productivity of the catalyst.

V. The arguments presented by the Respondent in the counterstatement filed on 9 November 1988 were first based on the non-obviousness of the two step activation of the catalyst precursor. Further, it was specified that the space time yield mentioned for Example 12 in Table III was wrong as a result of an erroneous conversion of lbs/hr/ft^3 into the corresponding metric units and that consequently the conclusions regarding this parameter drawn by the Appellant were not correct. As to the increase in titanium residue, it could not be regarded as a drawback since the level achieved was still perfectly acceptable from a practical point of view.

VI. The Appellant requests the impugned decision to be set aside and the patent revoked in its entirety.

The Respondent requests the appeal be rejected.

Reasons for the Decision

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

2. The patent in suit relates to a process for copolymerizing ethylene with one or more higher α-olefin monomers with magnesium and titanium containing complex catalysts in a gas phase fluid bed process. Although documents (3) and (4)

deal specifically with fluid bed reactor systems for the copolymerization of ethylene as will be discussed hereinafter, both the general catalyst features and the range of density of the polymers are so far from the means and aims contemplated by the Respondent that the Board, like the Opposition Division, regards document (2) as the closest prior art in the light of which the technical problem underlying the patent in suit should be determined.

This document describes a process suitable for the copolymerization of ethylene and higher α-olefins by means of a Ziegler catalyst composition prepared by activating with an aluminium compound a titanium catalyst compound obtained by first impregnating a porous silica carrier with a magnesium compound dissolved in an organic solvent, then treating the resulting solid compound with a titanium compound (Claim 1). This process can be carried out in virtually all relevant conventional embodiments, especially as dry-phase polymerization process (page 5, paragraph 4). Although the concept of electron donor is not used in this prior art document, the solvents actually used to dissolve the magnesium compounds (page 11, last five paragraphs) encompass most of the compounds listed as electron donors in the patent in suit (compare page 5, lines 59 to 65). These prior art catalysts lead to polymers with low catalyst residues; however, the bulk density of the resulting granules is regarded as too low for commercial purposes.

The technical problem underlying the patent in suit may thus be seen in providing a catalyst which would increase the bulk density of the polymer particles without impairing the low catalyst residues thereof to unacceptable levels.

According to the patent in suit this problem is solved essentially by a two step activation of the catalyst precursor which is impregnated in an inert porous carrier, the first step comprising treating the precursor composition outside the polymerization reactor in a hydrocarbon slurry with less than 10 mols of activator compound per mol of titanium compound in said precursor composition, the second step corresponding to a further activating treatment inside the polymerization reactor in such amounts as to provide from 10 to 400 mols of activator compound per mol of titanium compound in the precursor composition; as to the polymerization reaction it is carried out as a gas phase fluid bed process.

In the light of the results in Table I of the patent in suit (Examples 1 to 6) and in Table III of the reply filed on 28 May 1986 in opposition procedure (Examples 11 and 12), the Board is satisfied that the above defined technical problem is plausibly solved.

3. After examination of the cited documents the Board has concluded 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 has not been raised by the Appellant, it is not necessary to consider the matter in detail.

4. 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 (4).

4.1 Nothing in the preparation of the catalyst compositions specifically suitable for the polymerization of olefins in fluid bed reactors would suggest a two step activation of the catalyst precursor.

4.1.1 The supported catalysts described in document (3) are prepared by impregnation of bis(cyclopentadienyl)chromium (II) on an inorganic oxide having a large specific area, such as silica or alumina (page 3, paragraph 3 and Claim 13). The critical feature in this preparation is the drying step of the porous carrier before adsorption, which is necessary because of the sensitivity of the chromium compound to humidity; although in principle any temperature up to the sintering point could be suitable for that purpose, the actual temperature has a direct influence on the activity of the catalyst as well as on the molecular weight distribution and the melt index of the polymer (page 5, paragraphs 1 and 2). It is further specified that by an appropriate choice of the temperature of polymerization it is possible to control the molecular weight and thereby the melt index of the polymer (page 6, paragraph 2). However, there is no indication regarding a possible improvement of the bulk density.

4.1.2 A similar conclusion arises from document (4) which deals with a fluid bed reactor system and process employing a silyl chromate catalyst therein, either supported or unsupported, which gives rise to a solid particulate olefin polymer of low catalyst residue content (column 2, lines 9 to 21 and columns 3, lines 21 to 48). When incorporated in a porous support, the catalyst forms active sites on the surface and in the pores of the carrier; when a pore grown polymer becomes large enough, it ruptures the support thereby exposing fresh catalyst sites in the inner pores of the support (column 3, lines 49 to 62). This would appear to suggest a correlation between the size of the polymer particles and the structural features of the powder catalyst; however, even if the skilled man interpreted this teaching as an incentive to improve the bulk density by a better control of the size of the polymer particles, this could not lead to the solution claimed by the Respondent which lies in a specific activation of the catalyst precursor.

4.1.3 In summary, the documents directed to the fluid bed polymerization process do not teach how to control, let alone increase the bulk density of olefin polymers, and consequently cannot give the skilled man any hint for the solution of the above defined technical problem. In fact, as noted above, the densities which can be obtained by these fluid bed processes are generally higher than the range of 0.91 to 0.94 g/cm^3 contemplated by the Respondent and only the lower prior art densities would fall within this range. More specifically, the densities mentioned in document (3) are between 0.932 (Example 6) and 0.9745 (Example 8B) and those obtained according to document (4) between 0.9349 (Table I, Example 5) and 0.9748 (Table IV, Example 16). For this reason, it is even doubtful that the skilled man would consider these two teachings for the solution of the above defined problem.

4.2 The elemental analysis of the precursor catalysts according to Examples 1 and 7 of document (1) shows that the compositions thereof correspond respectively to $(Mg_{0.8}Ti_{0.2})\ Cl_{2.2}(THF)_{1.2}$ and $Mg_{0.63}Ti_{0.37}Cl_{2.74}(THF)_{2.45}$ wherein THF represents a tetrahydrofuran molecule. Although both formulae meet the quantitative requirements specified in Claim 1 of the patent in suit, there are substantial differences with regard to the latter as far as the preparation of the catalyst and the polymerization process are concerned.

First, the preparation of the catalyst according to document (1) does not involve the impregnation of the catalyst in and on an inert porous support. According to this disclosure the catalyst precursor is prepared either by coprecipitation from a mixture of ether complex solutions uniformly containing titanium and magnesium (column 4, lines 50 to 62) or by milling the mixture of an ether complex of titanium halide and an ether complex of magnesium halide in a ball mill (column 5, lines 15 to 18). The activation of the catalyst precursor occurs by simple contact with an organoaluminium compound (column 5, lines 22 to 28), but nothing in the description or the examples would suggest a partial activation outside the reactor followed by complete activation inside the reactor.

Besides, whereas according to the patent in suit the polymerization is carried out in a fluid bed reactor in gas phase, this reaction is performed in the prior art in an inert solvent as a slurry polymerization (column 5, lines 57 to 63).

In view of all these differences, it is evident that the mere fact that catalyst precursors within the scope of Claim 1 of the patent in suit are mentioned in document (1) does not make obvious the specific activation of these catalyst precursors and the operative features of the process claimed by the Respondent.

4.3 The partial activation of the catalyst precursor outside the reactor followed by the complete activation inside the reactor results in a marked increase in bulk density of the olefin polymer.

This improvement has been convincingly demonstrated in the additional Examples 11 and 12 filed by the Respondent. According to these examples, ethylene is copolymerized with butene-1 in presence of supported catalysts based on the same ingredients; in Example 12, which corresponds to the state of the art, a total activation of the catalyst precursor with triethyl aluminium is performed in the polymerization reactor whereas in Example 11, which corresponds to the process presently claimed, a two step activation of the precursor is carried out. The bulk densities of the granular copolymers are respectively 14.8 lbs/ft^3 or 0.237 g/cm^3 (Example 12) and 24.3 lbs/ft^3 or 0.389 g/cm^3 (Example 11) which corresponds to an increase of 64% of this parameter.

These two specific results are fully in line with the other experimental values mentioned in the patent in suit. The average value of the bulk densities of the polymers obtained by the process according to Claim 1 (Examples 1 to 3 and 7 to 10) is 0.360 g/cm^3 whereas it is only 0.252 g/cm^3 when the polymerization catalyst used was prepared by methods outside the scope of Claim 1 (Examples 4 to 6).

These results are in line as well with the figures obtained when other polymerization processes than the fluid bed reactor process are used. The values of bulk density disclosed in Examples 1, 2, 6 to 8 and 12 as well as in Comparative Example 3 of document (1) for various embodiments of slurry polymerization process show that this parameter ranges between 0.30 and 0.35 g/cm^3. A similar conclusion arises from the comparative Example filed by the Appellant on 22 August 1986 in opposition procedure; according to this test, which is carried out in an isobutane suspension system and on the basis of an arbitrary combination of features within the scope of document (2), the bulk density of the resulting copolymer is 0.345 g/cm^3. Even if some of the latter figures are comparable with the lower bulk densities reported for polymers obtained with catalysts within the scope of the patent in suit, the range of bulk density actually obtainable with the process claimed by the Respondent extends up to 0.5 g/cm^3 (patent in suit, page 3, line 45). That such high values of this parameter could be achieved by prior art methods has not been demonstrated by the Appellant.

Such an improvement obtained by operative features which cannot be derived from the prior art must thus be regarded as surprising and, therefore, inventive.

4.4 This higher bulk density results in many practical advantages. If a polymer of higher bulk density is to be stored or sold in granular form, smaller amounts of storage and shipping space are required for handling it; even if the polymer is pelletized prior to shipping, the processing of a given quantity of the high bulk density material through the pelletizing equipment requires significantly shorter processing times than would the same quantity of low bulk density materials, when using the same extrusion equipment.

Besides, the granular ethylene copolymer particles yielded by the process according to Claim 1 have a rounder shape, are more conducive to being fluidized in a fluid bed process and contain a relatively low level of fines (patent in suit, page 3, lines 46 to 48). This is evidenced by the results of screen analysis of the polymers according to Examples 1 to 6 which indicate that 32.16% by weight of the polymers prepared according to the patent in suit have an average particle size lower than 40 mesh (average for Examples 1 to 3) whereas this figure is 51.5% for the polymers prepared outside the scope of the patent in suit (average for Examples 4 to 6).

All these arguments in support of inventive step which were put forward in the counterstatement filed by the Respondent on 9 November 1988 have not been challenged by the Appellant.

4.5 It may be true that the higher bulk density is actually achieved at the expense of a higher titanium residue content, as apparent from Table III giving the experimental data for Examples 11 and 12. However, the Respondent put forward that the minor increase in the titanium residue of 2 to 3 ppm in Example 11 with regard to Example 12 is relatively insignificant and of no serious commercial disadvantage compared with the advantages obtained by the 64% increase in polymer bulk density. In absence of counterevidence provided by the Appellant who has the onus of proof, the Board accepts this argument, all the more as figures of the same order of magnitude (10 ppm), admittedly for another metal, are described in document (4) as low and compatible with a direct use of the polymer particles without specific treatment for catalyst removal (column 2, lines 36 to 40 and column 7, lines 44 to 52).

4.6 The argument of the higher space time yield indicated for Example 11 and of the resulting lower catalyst productivity is based entirely on an erroneous conversion of original units (lbs/hr/ft^3) into the corresponding metric system units (kg/h/m^3). According to Table III first submitted in examination procedure on 14 October 1983 and filed again in opposition procedure on 28 May 1986 the space time yield expressed in lbs/h/ft^3 is 3.6 for Example 11 and 5.2 for Example 12, thus lower in the case of a polymer prepared according to the patent in suit; these results have been confirmed at the appeal stage with the reply filed on 9 November 1988. It is self-evident that the space time yield cannot be respectively 57.6 and 23.2 kg/h/m^3 and that the last figure should read 83.2 kg/h/m^3. Compared with the space time yield measured in the other examples, this single value of 57.6 may appear rather low; however, a more significant comparison between the average value of this parameter when the process is carried out within and outside the scope of the patent in suit provides evidence that the two step activation of the catalyst precursor has no detrimental effect on the space time yield. The average space time yield for Examples 1 to 3 and 7 to 11 within the scope of the patent in suit is 88.8 whereas it is 79.5 for the Comparative Examples 4,5 and 12. This demonstrates that no negative conclusion can be drawn in this respect and that the process claimed by the Respondent solves the above defined problem without unacceptable side effects.

4.7 The patent in suit belongs to a series of patents relating to the so-called UNIPOL process for which the Respondent has been awarded the 1979 Kirkpatrick Chemical Engineering Achievement Award (Chemical Engineering, 3 December 1979, pages 80 to 85). The main feature of the UNIPOL process which enables the production of polymers of density as low as 0.918 to 0.920 is the drastic reduction in energy consumption and operating pressure which itself results in a startling compression in plant size (page 80, column 1, paragraph 2 and column 2, paragraph 5; page 81, column 1, paragraph 5). These significant advantages together with the higher bulk density presently achieved have to be appreciated in the context of the production of low density ethylene polymers by a fluid bed process. As stressed on page 83, column 2, paragraph 5, to bring such a fluid bed gas-phase low density polyethylene process to full commercial status required to solve specific problems connected with the fact that the difference between the melting point of the particles and the polymerization temperature is much narrower with low density polyethylene than with high density polyethylene. That this solution was not obvious was already noted above in point 4.1.3 when discussing the shortcomings of the prior art gas-phase polymerization processes according to documents (3) and (4) by which the low densities contemplated by the Respondent cannot be achieved.

4.8 In conclusion, for the reasons given above the two step activation of the catalyst precursor is a non-obvious modification in the preparation of catalysts suitable for the polymerization of olefins; this results in a marked increase in bulk density of the olefin polymer and involves, therefore, an inventive step.

5. These arguments apply equally to the dependent Claim 2 which merely represents a preferred embodiment of Claim 1.

Order

For the above reasons, it is decided that:

The appeal is dismissed.

The Registrar: The Chairman:

F. Klein K. Jahn

CG