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Bezeichnung der Erfindung:
Title of invention:
Titre de l'invention : Deactivation of catalyst in solution process for polymerisation of alpha-olefins

Klassifikation / Classification / Classement : C08F 10/00

ENTSCHEIDUNG / DECISION

vom / of / du 28 August 1989

Anmelder / Applicant / Demandeur :

Patentinhaber / Proprietor of the patent /
Titulaire du brevet : Du Pont Canada Inc.

Einsprechender / Opponent / Opposant : N.V. DSM

Stichwort / Headword / Référence :

EPÜ / EPC / CBE Articles 54, 56 EPC

Schlagwort / Keyword / Mot clé : "Novelty (yes) - Interpretation of a prior art document in the technological context of its date of publication"
"Inventive step (confirmed)"

Leitsatz / Headnote / Sommaire

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Case Number : T 613/88 - 3.3.1

D E C I S I O N
of the Technical Board of Appeal 3.3.1
of 28 August 1989

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Decision under appeal :
Decision of Opposition Division of the European Patent Office of 19 January 1988 posted on 12 October 1988 rejecting the opposition filed against European patent No. 0 062 127 pursuant to Article 102(2) EPC.

Composition of the Board :

Chairman : K. Jahn
Members : C. Gérardin
G.D. Paterson

Summary of Facts and Submissions

I. The mention of the grant of the patent No. 62 127 in respect of European patent application No. 81 304 965.7 filed on 22 October 1981 and claiming priority of 11 December 1980 of an earlier application in Great Britain, was published on 2 May 1985 on the basis of 9 claims.

Claim 1 reads as follows:

"A solution polymerization process for the preparation of high molecular weight polymers of α-olefins selected from the group consisting of homopolymers of ethylene and copolymers of ethylene and C_3-C_{12} α-olefins, said process comprising feeding monomer selected from the group consisting of ethylene and mixtures of ethylene and at least one C_3-C_{12} α-olefin, a coordination catalyst and inert hydrocarbon solvent to a reactor, polymerizing said monomer under solution polymerization conditions at a temperature of up to 320°C and a pressure of less than 25 MPa, deactivating the catalyst in the solution so obtained by admixing therewith a solution of a salt of an alkaline earth metal or zinc and an aliphatic monocarboxylic acid dissolved in hydrocarbon solvent, separating the hydrocarbon solvent and other volative matter from the resultant solution and recovering a composition comprising said high molecular weight polymer".

II. On 1 February 1986 the Appellant (Opponent) filed a notice of opposition requesting the revocation of the whole patent on the grounds that the subject-matter of the patent in suit was not novel and did not involve an

inventive step with regard to the teaching of mainly following documents:

(1a) NL-A-206 014 = (1b) GB-A-826 748
(2a) NL-C-84 948 = (2b) US-A-3 070 549
(3) US-A-4 105 609

In support of his counter-arguments the Respondent (Patentee) filed following documents:

(2c) GB-A-801 031 corresponding to documents (2a) and (2b)
(5) CA-A-660 869
(6) Ziegler-Natta Catalysts and Polymerizations by John Boor Jr., Academic Press, New York, San Francisco, London, 1979, pages 168-179
(7) Polymerization Processes by C.E. Schildknecht, John Wiley & Sons, New York, London, Sydney, Toronto, 1977, pages 369-373

III. By a decision delivered orally on 19 January 1988 with written reasons posted on 12 October 1988 the Opposition Division rejected the opposition on the grounds that the requirements of both novelty and inventive step were met. More specifically, it was stated in this decision that, although document (1b) which referred to document (2c) for the preparation of the polymer mentioned operative features of a solution polymerisation process, this could not be regarded as the disclosure of an actual solution polymerisation process, since this type of process was not known prior to document (5) whose priority dates were both subsequent to the priority dates of documents (1b) and (2c). As to the inventive step, it was pointed out that the mere fact that document (1b) in conjunction with document (2c) taught to overcome the problem of discolouration of polyethylene by addition of a metal salt

of a carboxylic acid, could not be regarded as an incentive to use such a compound to deactivate the catalyst, since the cause of discolouration was entirely different in the prior art.

IV. The Appellant thereafter lodged a notice of appeal on 8 December 1988 and paid the prescribed fee at the same time. In the Statement of Grounds filed on 20 February 1989 the Appellant first objected that not only document (1b) in conjunction with document (2c), but document (3) as well did teach the use of metal carboxylates for deactivating purposes in solution polymerisation processes. Although it was acknowledged that this particular process was not known prior to the disclosure of document (5), the skilled man would have immediately identified the features of the process according to documents (1b) and (3) at the priority date of the patent in suit as being peculiar to a solution polymerisation process; therefore, the subject-matter of the patent in suit was implicitly not novel. Further, these two teachings were relevant as well regarding the objection of lack of inventiveness of the solution claimed by the Appellant, since avoiding discolouration of the polymer in the prior art and deactivating the catalyst in the patent in suit were both achieved by addition of the same compound.

V. In his counter-statement filed on 12 June 1989 the Respondent put forward that the prior art processes, although they did involve the presence of solvent, were actually a slurry process in document (1b) and a high pressure solvent-free process in document (3). Because of the general features of these processes, one could not simply assume that the same compounds added in order to reduce or even eliminate the discolouration of a polymer would be suitable as catalyst deactivators when this

polymer was prepared by a solution polymerisation process. In fact, the interpretation of document (1b) in the light of the teaching of document (7) would rather suggest that the addition of carboxylate to polymers should be combined with the normal deactivation of the catalyst, not replace it.

Furthermore, the fact that in the patent in suit deactivation had to be carried out in homogeneous phase involved the choice of specific metal salts according to solubility criteria which did not exist in the prior art.

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, therefore, admissible.

2. First, the scope of documents (1b) and (3) has to be made clear with regard to the well known features of the various polymerisation processes as summarised in document (6).

2.1 According to the latter document the main requirement of a solution polymerisation process is that the polymer remains dissolved throughout the polymerisation; the catalyst, however, may be soluble or insoluble in the reaction medium (page 169, paragraph 1). Because of this condition of solubility, the temperature must be kept high

enough for the unreacted monomers and the polymer to remain in solution; in practice, the temperature depends on the structure of the polymer and the solvent selected (page 169, paragraph 2).

By contrast, in a slurry polymerisation process, almost all of the polymer separates as a distinct phase from the reaction solvent, i.e. as polymer particles (page 172, paragraph A, General comments on slurry process). For this reason, high temperatures must be avoided to prevent the polymer particles from fusing together.

Finally, in the vapour phase process or solventless process, an actual liquid phase is absent; this requires the polymer particles to be fluidised which is achieved by maintaining them in a suspension in the reactor. As to the catalyst components, they are usually introduced into the reactor in a small amount of an alkane solvent which becomes vapourised (page 173, paragraph 4 to page 174, paragraph 1, General comments on vapour phase process).

2.2 Document (1b) relates to a process of making moulded articles from polyethylene wherein 0.02 to 3 percent by weight of a salt of a metal selected from Groups II-A, II-B, and IV-B of the Periodic System and a fatty acid containing 8 to 24 carbon atoms or basic lead phthalate is incorporated and worked up by moulding (Claim 1). The low pressure polyethylene is obtainable by polymerising ethylene under relatively mild conditions of temperature and pressure as described for instance in GB-A-801 031 (page 1, lines 20 to 26), i.e. in document (2c). The addition of the salts inhibits the discolouration that otherwise occurs when polyethylene is heated to the moulding temperature and in addition inhibits the characteristic odour which is otherwise produced on moulding (page 2, lines 14 to 22); further, these

compounds diminish the corrosion of the metal parts that come in contact with the hot plastic mass during processing (page 2, lines 62 to 68) and even reduce the viscosity of the melts, which has a beneficial influence on the moulding operation (page 2, lines 79 to 87). Although the incorporation of the metal salt is usually carried out in mixers, kneaders, extruders or roll mills, i.e. into a polymer already prepared, it is possible to add the salt into the form of solution or suspension at some convenient stage during the preparation of the polymer (page 2, lines 52 to 61; Examples 1 and 2).

As mentioned above, the conditions of polymerisation are actually to be found in the reference document (2c) and are to be interpreted as peculiar to the slurry polymerisation process. According to this disclosure, the polymerisation reaction is conveniently carried out at relatively low pressures (page 3, lines 35 to 40) and in presence of an inert solvent, such as an aliphatic, cycloaliphatic or optionally halogenated aromatic compound or an ether, in such amounts that stirring of the reaction mixture is still possible towards the end of the reaction (page 3, lines 60 to 85 and Claim 10). According to Example 1, the reaction product consists of a solid cake of agglomerated polyethylene particles which is permeated with the solvent; after removal from the autoclave, the cake is kneaded with methanol, then with methanolic hydrochloric acid and washed with methanol and dried (page 3, lines 111 to 118). According to Example 3, the polymer separated has the appearance of a swollen jelly-like mass which is then first kneaded with methanol and thereupon freed from the solvent by a steam distillation in the presence of ordinary hydrochloric acid (page 4, lines 25 to 31).

2.3 Document (3) concerns a continuous process for the preparation of polyethylene involving pressures higher than 500 bars and temperatures higher than 160°C together with conventional Ziegler catalysts; the polymerisation is terminated by injecting into the reaction mixture a salt selected from the group consisting of alkali metal salts and alkaline earth metal salts of carboxylic acid in an amount sufficient to deactivate the catalyst (Claim 1). Whatever the type of the reactor, the working conditions are such that the reaction medium is homogeneous (column 2, lines 28 to 34); although it is even specified that the polymer is soluble in the reaction mixture, the general conditions of the polymerisation reaction, especially the absence of solvent in all the examples, are such that the process can only be regarded as a solvent-free process. This was pointed out by the Respondent in his counter-statement in reply to the Statement of Grounds of Appeal (page 3, point 7), and has not been disputed by the Appellant.

2.4 To sum up, the prior art processes referred to by the Appellant must be regarded as corresponding respectively to a slurry polymerisation process and a solventless process and can by no means be interpreted as solution polymerisation processes. As far as document (1b) is concerned, this conclusion was to be expected since the features of the solution polymerisation process were still unknown at the priority dates of this document and of the reference document (2c). Consequently, novelty of the subject-matter of the patent in suit can be acknowledged on the basis of the specificity of the solution polymerisation process.

3. In view of this conclusion, it seems consistent for the assessment of inventive step to start from the only document on file actually dealing with a solution

polymerisation process, namely document (5). According to Claim 1 as well as the description thereof (page 4, line 24 to page 5, line 21), both the reaction mixture and the polymer already formed remain dissolved in the hydrocarbon medium by a careful control of pressure and temperature parameters. At the end of the reaction, the product stream is withdrawn from the reactor through a pressure let-down valve into a product separator where the polymer with catalyst residues precipitates from the solution and is separated from the solvent and the unreacted ethylene gas, which are separately purified and recycled. The polymer obtained from the separation is then treated with methanol to remove the catalyst residues (page 14, lines 22 to 28).

In the light of this prior art the problem underlying the patent in suit may thus be seen in providing a simplified process wherein the removal of catalyst residues for purification purposes is no longer mandatory.

This problem is solved by deactivating the catalyst in the reaction medium solution at the end of the reaction by admixing a solution of carboxylic acid metal salt, as specified in Claim 1, dissolved in a hydrocarbon solvent directly with the polymerisation reaction product, separating all the volatile ingredients and recovering the polymer.

In view of the examples in the patent in suit the Board is satisfied that the above technical problem is plausibly solved.

4. The different methods disclosed in the prior art for non-solution polymerisation processes do not suggest the combination of operative features according to Claim 1.

4.1 The addition of specific carboxylic acid metal salts to polyethylene taught in document (1b), already discussed above in point 2.1, must be considered within the context of a slurry polymerisation process.

According to document (7) which concerns the slurry polymerisation of propylene or copolymerisation thereof with ethylene (page 369, paragraph 4), after unreacted monomer has been flashed out and recycled to the reactor, the catalyst is deactivated and solubilised by the addition of an alcohol, diketone or alkylene oxide. The bulk of the diluent and the solubilised catalysts are removed from the polymer particles by centrifugation, filtration or by aqueous extraction followed by centrifugation, and then the polymer is dried (page 370, paragraph 5). It is further specified that the level of catalyst residues should be as low as possible in the isolated polymer, since they may affect heat and light stability as well as colour. In addition, catalyst residues containing chlorides may cause mould corrosion during fabrication of the polymer or corrosion of metals that the polymer contacts during use; this can be overcome by the addition of antacids, such as calcium oxide and calcium stearate, in order to neutralise any residual chlorine in the polymer (page 373, paragraph 1).

The sequence of operations followed in document (1b) is exactly the same. As noted above, polyethylene moulded according to document (1b) is first prepared by the slurry polymerisation process described in document (2c) which in practice includes a post treatment of the polymer particles comprising basically kneading the polymer cake with methanol, treating the polymer with hydrochloric acid and drying the particles. The subsequent addition of the carboxylic acid metal salt according to document (1b) occurs thus on a polymer whose catalyst has already been

deactivated and solubilised by methanol; this means that in the prior art the metal salt is not added for deactivation purposes.

This interpretation is supported by the fact that in document (1b) it is specified that the metal salt may be added in the manufacture or work up, e.g. purification, of the polymer (page 2, lines 55 to 61). As the Respondent argued in opposition procedure (statement filed on 28 August 1986, page 2, paragraph 5), purification of the polymer would not include deactivation of the catalyst, but rather removal of solvent and various impurities.

For these various reasons, the addition of metal salts disclosed in document (1b) in combination with a previous deactivation of the catalyst with methanol and within the context of a slurry polymerisation process cannot lead to the solution polymerisation process presently claimed.

4.2 The same conclusion results from document (3) which, as stated above, describes a solvent-free polymerisation process wherein an alkali metal salt or an alkaline earth metal salt of carboxylic acid is injected into the reaction mixture. This reactant has the function of deactivating the two constituents of the catalyst, so that its reaction products with them remain in the polymer (column 1, lines 44 to 49; column 1, line 67 to column 2, line 2). The salt can be injected in the molten state or in suspension or in solution in a hydrocarbon (column 3, lines 5 to 7). From these various embodiments it is clear that the prior art failed to recognise the criticality of the solubility in the hydrocarbon mentioned in the patent in suit (column 3, lines 42 to 50) as well as the particular effectiveness of the alkaline earth metal salts in combination with a solution polymerisation process.

This is quite apparent from the comparative data provided in Appendix I "Effect of deactivator on colour of polymer" filed together with the counter-statement in opposition procedure on 28 August 1986. Whereas the Tables of document (3) show that satisfactory contents of catalyst metal residues can be obtained with calcium stearate, the above Appendix shows that this compound leads to totally unacceptable levels of catalyst residues with a solution polymerisation process, as evidenced by the poor colour rating of the polymer (runs 2 and 3); likewise, the difference in deactivating effectiveness between calcium stearate and calcium caprylate (run 6) was not to be expected in view of the broad definition of the deactivators in document (3) (column 2, line 65 to column 3, line 5). Both results illustrate the fact that effective deactivation in a solution polymerisation process require the whole system to be homogeneous, which is not suggested by the prior art (column 3, lines 5 to 7). Similarly, whilst sodium stearate, naphthoate and benzoate give results comparable to alkaline earth metal salts in the prior art solventless polymerisation process, the alkali metal salts are unsuitable in the solution polymerisation process presently claimed (run 8), which again is unexpected. Furthermore, nothing in the prior art would suggest to use soluble zinc salts in combination with a solution polymerisation process.

4.3 In conclusion, neither the features of the slurry polymerisation process wherein a combination of deactivating step and neutralising step is required, nor the features of the solventless polymerisation process wherein a broad class of deactivators are mentioned as equally suitable and the deactivating effect does not depend on the physical state thereof, can suggest the use of a small group of salts specifically soluble in the reaction medium

in a solution polymerisation process. For this reason, the subject-matter of Claim 1 involves an inventive step.

5. Claim 1 being allowable, the same applies to dependent Claims 2 to 9 which merely represent preferred embodiments of Claim 1 and whose patentability is supported by that of the main claim.

Order

For these reasons, it is decided that:

The appeal is dismissed.

The Registrar: The Chairman:

F. Klein K. Jahn

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