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D E C I S I O N
of 12 July 2000

Case Number: T 0892/97 - 3.3.3

Application Number: 91116958.9

Publication Number: 0479306

IPC: C08G 69/00

Language of the proceedings: EN

Title of invention:

Preparation of polyamides from omega-aminonitriles

Applicant:

E. I. DU PONT DE NEMOURS AND COMPANY

Opponent:

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Headword:

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Relevant legal provisions:

EPC Art. 54, 56

Keyword:

"Novelty - (yes) after amendment"

"Inventive step - non-obvious combination of features"

Decisions cited:

T 0606/89, T 0795/93

Catchword:

-



Case Number: T 0892/97 - 3.3.3

D E C I S I O N
of the Technical Board of Appeal 3.3.3
of 12 July 2000

Appellant:

E. I. DU PONT DE NEMOURS AND COMPANY
1007 Market Street
Wilmington
Delaware 19898 (US)

Representative:

Jones, Alan John
CARPMAELS & RANSFORD
43 Bloomsbury Square
London WC1A 2RA (GB)

Decision under appeal:

Decision of the Examining Division of the
European Patent Office dated and issued in
writing on 21 March 1997 refusing European patent
application No. 91 116 958.9 pursuant to
Article 97(1) EPC.

Composition of the Board:

Chairman: C. Gérardin
Members: B. ter Laan
A. Lindqvist

Summary of Facts and Submissions

- I. European patent application No. 91 116 958.9, filed on 4 October 1991, claiming priority from an earlier application in the USA (US 591191 of 4 October 1990) and published on 8 April 1992 under No. 0 479 306 (Bulletin 92/15), was refused by a decision of the Examining Division of the European Patent Office dated 21 March 1997. That decision was based on a set of six claims filed on 28 February 1996, claim 1 reading:

"A process for the preparation of polyamide which comprises heating a mixture comprising an omega-aminonitrile, water, and an oxygenated phosphorus catalyst at a pressure in the range of 1328 to 2412 kPa (200 to 350 psig), and when the temperature reaches 200 degrees C to 260 degrees C, adding water continuously at a rate of from 10 to 50 grams per hour per 100 grams of omega-aminonitrile initially present in the mixture and after the temperature is above 240 degrees C continuously removing water vapour and ammonia from the reactor, and maintaining the temperature in the range of 240 degrees C to 310 degrees C until 15 to 75 grams of water has been added per 100 grams of omega-aminonitrile initially present in the mixture, then stopping the water addition, and polymerizing the resulting mixture at a temperature in the range of 240 degrees C to 330 degrees C until polyamide having a number average molecular weight of at least 10,000 is formed."

Dependent Claims 2 to 6 referred to preferred embodiments of the process according to Claim 1.

II. The Examining Division held that the claimed subject-matter did not satisfy the requirements of Articles 54 and 84 EPC and that, although not grounds for the decision, Articles 56 and 123(2) EPC were also not complied with.

In particular, it was held that

- (a) Regarding Article 84 EPC, the amount of water initially present during the polymerization was not mentioned in the claims, in spite of the fact that from the description it appeared to be an essential feature of the invention.
- (b) As regards novelty, D2 (US-A-4 568 736) described the removal of ammonia by having it enter the vapour phase under conditions which inevitably would also lead to the evaporation of water, so that the claimed subject-matter lacked novelty.
- (c) Regarding inventive step, D1 (DE-A-3 534 817) differed from the claimed subject-matter in the temperature range at which the water was added. However, since no comparative examples were given to support a technical effect, the problem to be solved could only be formulated as to define a further process for preparing polyamides by reacting omega-aminonitriles. It was, however, obvious to choose any of the process variations known in the art, e.g. as disclosed in D1 and D2. The additional experiments presented in the declaration filed with the letter of 28 February 1996 were not suitable to change that view as they did not form a proper comparison with the state of the art.

III. On 22 May 1997 a Notice of Appeal was lodged against that decision, together with payment of the prescribed fee. With the Statement of Grounds of Appeal filed on 25 July 1997, the Appellant (Applicant) submitted two new sets of claims, which were replaced by six new requests on 6 June 2000.

IV. At the oral proceedings before the Board, held on 12 July 2000, in which several objections under Article 84 EPC were raised, those claims were replaced by two sets of six claims each as main and auxiliary requests. Claim 1 of the main request reads as follows:

"A process for the preparation of polyamide which comprises heating in a reactor a mixture comprising an omega-aminonitrile, from 1 to 50% by weight of the mixture of initial water, and from 0.05 to 0.3% by weight relative to the aminonitrile of an oxygenated phosphorus catalyst at a pressure in the range of 1379 to 2413 kPa (200 to 350 psig), and when the temperature reaches 200°C to 260°C, adding water continuously at a rate of from 10 to 50 grams per hour per 100 grams of omega-aminonitrile initially present in the mixture, said continuous addition of water being performed during the first 0.5 to 1.5 hours of the polymerization, and after the temperature is above 240°C continuously removing water vapour and ammonia from the reactor, and maintaining the temperature in the range of 240°C to 310°C and the pressure in the range of 1379 to 2413 kPa gauge (200 to 350 psig) until 15 to 75 grams of water have been added per 100 grams of omega-aminonitrile initially present in the mixture, then stopping the water addition, and finally polymerizing the resulting mixture at a temperature in

the range of 240°C to 330°C and a pressure in the range of 13 to 25 atmospheres until polyamide having a number average molecular weight of at least 10,000 is formed." (Amendments to the claim as originally filed are indicated in bold by the Board).

Dependent Claims 2 to 6 refer to preferred embodiments of the process according to claim 1.

The Appellant's arguments, submitted in writing and during oral proceedings, can be summarised as follows:

- (i) As regards Article 84 EPC, the process comprised two steps: in the first stage the -CN group was hydrolysed, which reaction required the presence of water. In the second step polymerization took place which was a condensation reaction giving rise to the production of water. According to the invention, the reaction conditions should be chosen such that a dynamic process ensued in which purging through water occurred, resulting in fast hydrolysis and purging of yellowing products. This was effected by carrying out the reaction at a relatively low pressure at the start so that the water could boil off, to be replaced by newly added water, or, in other words, by continuously adding and removing water during the first reaction stage. The wording of present Claim 1 reflected that process correctly and gave all necessary details. In particular, the steps of (a) mixing, (b) heating, (c) adding water when the temperature reaches 200 to 260°C, (d) then either increasing the temperature to 240°C and starting venting or venting immediately if the temperature is already 240°C or higher, (e) continuing the addition of water and venting until the required amount of water is reached,

(f) stopping water addition and (g) polymerizing until the polymer reaches a molecular weight of at least 10,000, as demonstrated in the example, were clearly defined by the present wording of Claim 1.

- (ii) As to novelty, D2 disclosed temperature/pressure conditions at which the ammonia was boiled away but the higher boiling water was retained, whereas the claimed subject-matter called for conditions at which the water also boiled off. Although a temperature range of 200 to 300°C and a pressure range of 200 to 800 psig were indicated, which overlapped the present ranges, the document clearly stated that the ammonia generated during the reaction was progressively removed, whereas the water was only removed at the end of the polymerization. Accordingly, in the examples a temperature of 250 to 260°C and a pressure of 750 psig were used, in which conditions only the more volatile ammonia was evaporated, not the water. Therefore, the combination of temperature and pressure as now required, which allowed both water and ammonia to be removed, had not been disclosed.

D1 had not been cited by the first instance against novelty. It did not disclose the specific rate at which the additional water should be added, nor its addition at an early reaction stage.

The Appellant concluded that the claimed subject-matter was novel.

(iii) Regarding inventive step, the problem solved was to define a process in which the polyamide was formed quicker and with a reduced yellowness index. This was achieved by the continuous injection of additional water while maintaining the reaction mixture at a relatively high temperature and low pressure, such that the reaction mixture was below the vapour pressure of the water. The example showed that this combination of features was effective for the solution of the above-mentioned problem.

D2 taught to prevent water escaping from the reactor by maintaining a high pressure, not by continuous injection. Additional experiments showed an improved yellowness of the present products. Starting from D1, the present process was much more rapid, presumably because the water content of the reactor in D1 was too high, and the product was also expected to be less yellow. D1 did not suggest that the rate of polymerization could be improved by a water injection process as now claimed. Since the combination of water addition known from D2 with the process described in D1 did not result in any particular technical effect, there was no incentive to combine those documents. Hence the claimed subject-matter was inventive.

VI. The Appellant requested that the decision of the first instance be set aside and that a patent be granted based on Claims 1 to 6 of the main request or, alternatively, Claims 1 to 6 of the auxiliary request.

Reasons for the Decision

1. The appeal is admissible.

The wording of the claims

2. With respect to the wording of Claim 1 as originally filed, the present version differs by (i) the requirement that the reaction mixture should be heated in a reactor, (ii) the amount of initial water present in the reaction mixture, (iii) the amount of catalyst, (iv) the period of time during which the water should be added, (v) the pressure range at which the water addition is performed, (vi) the addition of the word "finally" and (vii) the pressure at which the final or post-polymerization is carried out.
 - 2.1 The added requirement that the mixture should be heated in a reactor is, in view of the reaction conditions such as temperature and pressure as required in Claim 1 and the further details given in the whole of the description, self-evident and does not extend beyond the content of the application as filed.
 - 2.2 The amount of initial water is disclosed on original page 3, lines 14 to 21.
 - 2.3 The amount of catalyst is supported by original page 3, lines 28 to 30.
 - 2.4 The time period during which water addition takes place is described on page 2, lines 32 to 35.
 - 2.5 The pressure range at which the temperature is maintained at 240°C to 310°C and during which the required amount of water is added, is disclosed on original page 2, lines 14 to 16.

- 2.6 The word "final", which supports the term "finally polymerizing", can be found on original page 4, line 1.
- 2.7 The pressure range at which the final polymerization should be carried out is indicated on original page 4, lines 7 to 9, which passage follows the information contained in lines 1 to 6, and also refers to the final polymerization, so that the combination of temperature and pressure is allowable.
- 2.8 The wording of dependent claims 2 to 6 has not been amended.
- 2.9 Therefore, the Board is satisfied that the requirements of Article 123(2) EPC are fulfilled.
3. The present wording of the claims also meets the requirements of Article 84 EPC in terms of clarity and support by the description. In particular, the conditions for the continuous addition and evaporation of water, which are essential features of the claimed process, are now clearly defined. The possibilities of first adding water at a temperature of below 240°C, heating to 240°C and then evaporating water, as well as directly heating the mixture to a temperature of above 240°C, so that water evaporation may start before or simultaneously with water addition, are clearly included.

Novelty

4. The Examining Division held that D2 destroyed the novelty of the claimed subject-matter.
- 4.1 D2 discloses a process for the production of a solid polyamide comprising contacting an omega-aminonitrile, water and a catalytic amount of an oxygen containing phosphorus compound (Claim 1). In particular, it

concerns a two stage process wherein the first stage comprises maintaining a temperature of between 200° to 300°C and a pressure of between 200 and 800 psig for a period of time sufficient to form low molecular weight polyamides, and wherein the second stage comprises maintaining the temperature at 265° to 295°C and gradually reducing the pressure to less than or equal to atmospheric pressure (column 4, line 43 to column 5, line 8).

- 4.2 The role of water during that process is extensively described in column 3, line 56 to column 4, line 18. Typically a stoichiometric excess is employed during the polymerization, though that amount of water is not necessarily present at all times. The initial amount of water preferably does not exceed 35%, more preferably 15%, by weight of the total weight of the reaction mixture. Then, as the polymerization proceeds, additional water is gradually added. That amount should be kept at a minimum since the water will have to be removed from the reaction product at the end of the polymerization and less energy is then required for the process.
- 4.3 In one embodiment, the ammonia, which is a by-product of the reaction, is removed continuously, but all of the water is retained and eventually removed after the hydrolysis of the aminonitrile is essentially complete (column 4, lines 33 to 42).
- 4.4 The temperature/pressure profile during polymerization is described in column 4, line 43 to column 5, line 8. Typically, in the production of nylon-6, in a first stage the temperature is maintained at 200 to 300°C under autogenous pressure (typically 200 to 800 psig) for sufficiently long to form low molecular weight polyamides. Ammonia is removed from the reaction vessel while maintaining the water concentration at a level

sufficient for the reaction to proceed (typically more than 14 weight percent). After completion of the first stage, the pressure is gradually reduced to atmospheric or subatmospheric and the temperature raised to 260 to 295°C.

In Example II the reaction mixture is heated at 250 to 260°C and the ammonia vented at 750 psig pressure. After 3.5 hours the pressure is lowered and the temperature raised to or held at 260°C and the low molecular weight polyamides are combined to form the final product.

4.5 Although the temperature range of 200 to 300°C and the pressure range of 200 to 800 psig for the first step of the polymerization disclosed by D2 encompass the now claimed values of 200 to 260°C and 200 to 350 psig, the latter ranges are not disclosed as such. In view of the clear statement that ammonia is evaporated whereas the water is retained until the completion of the first stage of the reaction (column 4, lines 7 to 9, 33 to 42 and 62 to 65) and the high pressure actually used in the examples (750 psig at a temperature of 250 to 260°C), D2 cannot be considered to disclose the combination of pressure and temperature, and hence the addition and evaporation of water, now required.

4.6 It follows that the process according to D2 does not describe the combination of features specified in Claim 1 of the application in suit, so that novelty is acknowledged.

Inventive step

5. The application in suit concerns the preparation of polyamides from omega-aminonitriles. Such processes are disclosed in both D1 and D2. The Examining Division considered D1 as the closest document.

5.1 D1 discloses a process for the direct, stepwise preparation of linear polyamides from omega-aminoalkylnitriles, the alkyl groups having at least 4 carbon atoms, and excess water at a high temperature and a pressure higher than atmospheric, characterized in that the reaction is carried out continuously or discontinuously in the presence of catalytically active compounds which either remain in the reaction product or may be removed by simple washing with water (Claim 1).

According to the detailed description of the process, 5 parts by weight of ϵ -aminocapronitrile, 1 part by weight of water and 0.01 parts by weight of catalyst are heated to a temperature of 245°C and a pressure of e.g. 25 bar. After approximately 3 hours ammonia is no longer formed and the temperature has risen to about 270°C. Then 1.5 parts by weight of water are added in order to remove residual ammonia. Then, the pressure is reduced stepwise, which is accompanied by the removal of excess water. Over a consecutive time of 7 to 10 hours the resulting polyamide melt may then be converted to a high molecular weight polymer (page 4, lines 45 to 59).

In the Examples 1 to 11, 30 parts by weight of ϵ -aminocapronitrile, 8 parts by weight of water and a number of catalyst in various amounts are heated to a temperature of 245°C and a pressure of 23 to 25 bar within 45 minutes. After 180 minutes the gas formation has stopped and 1.8 parts by weight of water are added while maintaining the pressure. After reducing the pressure to atmospheric, the polyamide is post-condensed. In Example 12, 1000 g ϵ -aminocapronitrile, 220 g water, 118 g caprolactam oligomers, 80 g regenerated caprolactam, a catalyst and a chain regulator are heated to a temperature of 245°C and a pressure of 26 bar in 50 minutes. After 190 minutes,

during which the temperature increases to 275°C, the gas formation has stopped and 50 ml water are added while keeping the pressure constant. Water and ammonia vapour evaporate. After reducing the pressure to atmospheric, during which ammonia containing water vapour escapes, the polyamide is post-condensed.

5.2 According to the description of the application in suit the object of the invention is to provide a high quality polymer of good colour and of high molecular weight in a relatively short reaction time (page 2, lines 7 to 10). Both D1 and D2 aim at a high molecular weight polyamide; however, neither of those documents is concerned with a short reaction time or the colour of the product. In general, a document serving as the starting point for evaluating the inventive merits of an invention should relate to the same or a similar technical problem or, at least, to the same or a closely related technical field as the application in suit (see decisions T 606/89 of 18 September 1990 and T 795/93 of 29 October 1996; both unpublished in OJ EPO). Therefore, neither of D1 or D2 qualifies as a proper starting point for the evaluation of the inventive merits of the claimed subject-matter.

5.3 Nevertheless, for the sake of the present decision, the Board will follow the approach adopted by the Appellant during oral proceedings and, consequently, regard the technical problem underlying the application in suit as the definition of an improved process for the preparation of high molecular weight polyamides, the improvement being in the efficiency of the polycondensation reaction and in the colour of the polymer.

5.4 According to the patent in suit that problem is solved by the combination of measures defined in Claim 1, in particular the controlled amount of water and adjustment of the physical reaction conditions.

5.5 From the example in the application it can be seen that the reaction time needed to produce high molecular weight polyamides according to the application in suit is in fact shorter than that for both of D1 and D2. Furthermore, the additional example filed during the examination proceedings (letter of 28 February 1996), demonstrates that the colour of the product is also improved over that of the product according to D2. Therefore, it may be concluded that the various aspects of the above-defined technical problem are effectively solved.

6. It remains to be decided whether the claimed subject-matter is obvious having regard to the documents on file.

6.1 The general teaching of D1 is that the first part of the reaction is carried out in the presence of a relatively small amount of water (about 20% by weight of the aminonitrile) and that only after the formation of ammonia has stopped, after about 3 hours, a further relatively small amount of water is added. There is no suggestion to add water during the first 0.5 to 1.5 hours of the reaction, as now required.

Therefore, D1 by itself does not render the present combination of features obvious.

6.2 The same is valid for D2, since the general teaching is to retain all the water during the first reaction stage and to add as little water as possible later, in order to avoid the necessity of removing large amounts of water, which is energy consuming.

- 6.3 Since neither of the documents provides an incentive to add water during the first stage of the polymerization, a combination of D1 and D2 would also not lead to the now claimed process, in which the addition of water during the first stage is an essential feature.
- 6.4 For the above reasons, the Board comes to the conclusion that the subject-matter of Claim 1 involves an inventive step.
7. As Claim 1 of the main request is allowable, the same goes for dependent Claims 2 to 6, the patentability of which is supported by that of claim 1.
8. Since the main request is allowed, the auxiliary request needs not be considered.
9. Although the claims according to the main request fulfil the various requirements of the EPC, a patent cannot be granted according to the Appellant's request in view of the necessity to adapt the description to the amended claims. To that end, the case has to be remitted to the Examining Division.

Order


For these reasons it is decided that:

1. The decision under appeal is set aside.
2. The case is remitted to the Examining Division with the order to grant a patent on the basis of Claims 1 to 6 filed as main request during oral proceedings, after any consequential amendment of the description.

The Registrar:


E. Gorgmaier

The Chairman:


C. Gérardin