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DECISION
of 18 April 1997

Case Number: T 1014/93 - 3.3.3

Application Number: 88303191.6

Publication Number: 0286444

IPC: C08G 63/18

Language of the proceedings: EN

Title of invention:
Process for producing a liquid crystalline polyester of a cyclohexanedicarboxylic acid and an aromatic diol

Patentee:
CHISSO CORPORATION

Opponent:
-

Headword:
-

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step (no) - obvious combination of known features"

Decisions cited:
-

Catchword:
-

Case Number: T 1014/93 - 3.3.3

DECISION
of the Technical Board of Appeal 3.3.3
of 18 April 1997

Appellant:

CHISSO CORPORATION
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Osaka-fu (JP)

Representative:

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Decision under appeal:

Decision of the Examining Division of the European Patent Office posted 22 July 1993 refusing European patent application No. 88 303 191.6 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: C. Gérardin
Members: H. H. Fessel
J. A. Stephens-Ofner

Summary of Facts and Submissions

I. The European patent application No. 88 303 191.6 filed on 8 April 1988 was refused by a decision of the examining division 2.1.02.012 of the European Patent Office dated 22 July 1993.

That decision was based on claims 1 to 4 as originally filed, claim 1 reading as follows:

"A process for producing a polyester which comprises condensing a cyclohexanedicarboxylic acid and an aromatic diol using, as condensing agent, thionyl chloride and pyridine in combination."

Claims 2 to 4 concerned preferred embodiments of the process according to claim 1.

II. The reason for the decision was that the subject-matter as claimed in claim 1 did not involve any inventive step **vis-à-vis** the teaching given in the following prior art documents:

D1: J. Polymer Science, Polymer Chem. Ed. Vol. 24 (1986), pp. 1697-1701;

D2: J. Polymer Science, Polymer Chem. Ed. Vol. 24 (1986), pp. 97-102;

D3: US-A-4 355 133;

D4: US-A-4 327 206 and

D5: US-A-3 143 526.

More specifically, it was stated that the alleged improved properties had not been demonstrated and that the problem effectively solved reduced to the provision of a further process to produce a polymer already known from D3, D4 and D5. The solution of this problem was regarded as obvious in view of the teaching of D1 and D2, which both disclosed the use of a combination of thionyl chloride and pyridine as condensing agent in a process for producing aromatic polyesters.

III. On 21 September 1993 a notice of appeal was lodged against that decision together with payment of the prescribed fee. The statement of grounds of appeal was filed on 19 November 1993.

(i) Together with that statement the appellant submitted as main request the set of claims filed originally wherein claim 2 had been slightly amended (referred to as "Annexe A") and as auxiliary request a new set of 7 claims (referred to as "Annexe B"), of which claim 1 reads as follows:

"A process for producing a polyester derived from a cyclohexane dicarboxylic acid and an aromatic diol, which process comprises the steps of:

(i) forming a condensing agent comprising thionyl chloride and pyridine;

(ii) adding to the condensing agent, in steps, a cyclohexane dicarboxylic acid and an aromatic diol; and

(iii) polycondensing the resulting mixture whereby to obtain the desired polyester."

Claims 2 to 7 are directed to preferred embodiments of the process according to claim 1.

(ii) In substance the appellant disputed the relevance of D1 and D2 to a process involving the use of cycloaliphatic compounds. More specifically, D1 summarized the latest results of a study first reported in D2 about the preparation of polyesters by the direct polycondensation method; the information provided by these documents when read together clearly showed that, whilst a thionyl chloride/pyridine system was an effective polycondensation agent for aromatic dicarboxylic acid/aromatic diol systems, it did not appear to work for aromatic dicarboxylic acid/cyclohexane diol systems. A skilled person would thus consider the cyclohexane moiety as the most important factor in the aromatic dicarboxylic acid/cyclohexane diol system and, therefore, expect the direct polycondensation method known from D1 and D2 to fail with cyclohexanedicarboxylic acid.

(iii) During oral proceedings held on 18 April 1997, after having been informed that the wording of both sets of claims was not objectionable under Article 123(2) EPC, the appellant argued along the line of an improvement of the polyesters described in D5 regarded as the closest state of the art. The polymers obtained in examples 1 to 9 were said to have inherent viscosities of at least 0.55, but generally not much greater than 1.0. The figure of 2.0 mentioned in column 4, line 56 was thus more an expectation or hope than the more realistic values actually achieved in the worked examples. The technical problem underlying the present application had consequently to be seen in an improvement of the product obtained in D5. On that basis there was no reason to consider a combination of the teachings of D1 and D2.

IV. The appellant requested that the decision under appeal be set aside and that a patent be granted on the basis of claims 1 to 4 referred to "Annexe A" as main request or on the basis of claims 1 to 7 referred to "Annexe B" as auxiliary request, both filed on 19 November 1993.

Reasons for the Decision

1. The appeal is admissible.

Main request - Article 123(2) EPC

2. The only amendments with respect to the original set of claims concern claim 2, wherein (i) the expression "aromatic oxycarboxylic acid" has been replaced by "aromatic hydroxycarboxylic acid", and (ii) the expression "co-condensedwith" has been changed into "co-condensed with". Since the former amendment has no impact on the definition of the acid and the latter is merely of an editorial nature, the requirements of Article 123(2) EPC are met.

Novelty

3. The Board concurs with the Examining Division that the requirements of Article 54 EPC are also met, since none of the documents on file discloses the preparation by direct polycondensation of a polyester from a cyclohexanedicarboxylic acid and an aromatic diol using a combination of thionyl chloride and pyridine as a condensing agent.

Documents D3 to D5

4. As acknowledged by the appellant both in the application in suit (page 2, lines 14/15) and in the statement of grounds of appeal (page 2, paragraph 4), polyesters comprising units derived from a cyclohexanedicarboxylic acid and aromatic diols are well known.

4.1 D3 describes copolyesters which consist essentially of four specific recurrent units, namely 6-oxy-2-naphthoyl moieties (I), 4-oxybenzoyl moieties (II), 1,4-dicarboxycyclohexane moieties (III) and symmetrical dioxyaryl moieties (IV) (claim 1). This combination of units is responsible for anisotropic properties in the melt (column 3, lines 4 to 29). These copolyesters commonly exhibit an inherent viscosity of at least 1.0 dl/g, in practice up to 9.0 dl/g, when dissolved in a concentration of 0.1 percent by weight in pentafluorophenol at 60°C (column 7, lines 32 to 37).

Whether a melt acidolysis procedure or a slurry procedure is adopted for the preparation of the polymer, the compounds giving rise to moieties (I), (II) and (IV) are suitably used in the esterified form, especially as acetate esters (column 8, lines 3 to 48). Catalysts suitable in either procedure comprise conventional tin and titanium derivatives, alkali and alkaline earth metal salts of carboxylic acids as well as Lewis acids (column 8, lines 49 to 56). The molecular weight of the polyester may be further increased by subjecting the polymer to a solid state post-polymerisation step (column 8, lines 61 to 68).

4.2 The transesterification method is also used in D4 according to which (1) at least 50 mole percent of an alkyl or aryl diester of trans-1,4-cyclohexanedicarboxylic acid, (2) up to 50 mole percent of a diester of an aromatic dicarboxylic acid, and (3) at least one diacyl ester of an aromatic diol are reacted in the presence of an ester exchange and polymerisation titanium or tin catalyst (claims 1 and 4). The molecular weight may be further increased by solid phasing this prepolymer at about 300°C, whereby inherent viscosities higher than 0.6 are achieved (claim 7; column 3, lines 42 to 45; example 3).

4.3 The polyesters described in D5 are obtained by ester-interchange reaction from a trans-1,4-cyclohexanedicarboxylate diester, optionally together with a diester of another dicarboxylic acid, and one or two specific aromatic diols in the presence of a conventional catalyst (claim 1 in conjunction with column 2, lines 24 to 30 and column 3, lines 49 to 71). The resulting prepolymer is suitably built up by the solid phase process to increase the inherent viscosity to at least 0.55 (column 2, lines 32 to 35; column 3, lines 71 to 73; column 4, lines 52 to 59).

4.4 Thus the common feature of these processes is the use of the transesterification method, e.g. a conventional procedure using well known catalysts wherein the monomer reactants are provided in the esterified form, normally followed by a solid state post-polymerisation step to increase the molecular weight.

Problem and Solution

5. The application in suit concerns a process for producing a liquid crystalline polyester of a cyclohexanedicarboxylic acid and an aromatic diol.

5.1 The excessively low thermal deformation temperature of such polymers reported in the introduction of the application in suit (page 2, lines 19/20) and the arguments presented by the appellant during oral proceedings in connection with the values of inherent viscosity achievable by the process as claimed make it necessary to consider the experimental evidence actually available in order to define the technical problem.

5.1.1 Thus according to the application in suit, liquid crystalline polyesters derived from cyclohexanedicarboxylic acid tend to have a rather low thermal deformation temperature and, consequently, inadequate heat resistance. As pointed out by the Examining Division in its decision (cf. reasons, point 4.1, third paragraph), there is no experimental evidence in the application in suit that the polyesters obtainable by the process described therein are superior in that respect.

In view of the high heat distortion temperature mentioned in D5 (column 1, lines 14 to 16 and 27 to 31), in particular the values reported in the table of column 4 (examples 1 to 4) which offer a most adequate basis of comparison, it was necessary to consider this parameter in detail in the application. In the absence of any appropriate comparison with this prior art, heat resistance cannot be considered for the definition of the technical problem.

5.1.2 In a further attempt to define the technical problem in positive terms the appellant relied on the values of inherent viscosity disclosed in examples 1 to 3 of D5, which range between 0.99 and 0.72 (column 4, lines 56 to 59), and argued that the problem underlying the application in suit had thus to be seen in the definition of a process giving rise to polyesters having higher inherent viscosities.

This approach cannot be accepted by the Board for the following reasons. First, apart from the fact that there is no explicit lower limit of inherent viscosity

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in claim 1 of the application in suit, the values actually achieved in examples 1, 5, 6, 8, 12, 22 to 30, 43, 44 and 46, in other words in 17 examples out of 46, are also all lower than 1.0; thus, even if an inherent viscosity as high as 4.2 is reported in the case of example 11, this extreme value cannot be regarded as significant since the corresponding process features are not incorporated in claim 1. Secondly, the fact cannot be ignored that the polyesters obtained in D3 prior to heat treatment exhibit inherent viscosities up to 9.0 dl/g (column 7, lines 32 to 37) and that these polyesters, like those according to the application in suit, form an atypical optically anisotropic melt phase at a temperature below 350°C, e.g. exhibit liquid crystalline properties (column 3, lines 4 to 29). Thus, as pointed out by the Board during oral proceedings, if a difference were at all to be made between the three documents D3 to D5, D3 should rather be regarded as the closest state of the art.

5.2 In the absence of any evidence of improvement in terms of heat resistance and/or inherent viscosity, the problem underlying the application in suit can only be seen in the definition of an alternative process for producing liquid crystalline polyesters derived from cyclohexanedicarboxylic acid.

5.3 According to the application in suit this problem is to be solved by condensing a cyclohexanedicarboxylic acid and an aromatic diol using as condensing agent a combination of thionyl chloride and pyridine, e.g. by using a direct polycondensation procedure.

5.4 In view of the numerous examples in the application in suit, which show that polyesters having both satisfactory inherent viscosities and liquid crystalline properties can be obtained, the Board is satisfied that the above defined technical problem is effectively solved.

Inventive step

6. It remains to be decided whether the claimed subject-matter would have been obvious to a person skilled in the art having regard to the documents on file.

6.1 It is evident that D3 to D5, which all rely specifically on the transesterification method to prepare polyesters, irrespective of whether a melt acidolysis procedure or a slurry procedure is used, and, further, whether this reaction is followed by a final solid state polymerisation step or not, cannot provide any incentive to use the direct polycondensation method, let alone under the particular conditions required in claim 1 of the application in suit.

6.2 D1 is an article concerning the direct polycondensation of hydroxybenzoic acids, optionally together with aromatic dicarboxylic acids and bisphenols, which is carried out in the presence of thionyl chloride in pyridine, whereby aromatic polyesters of high inherent viscosity up to 3.8 respectively 5.6 can be obtained (page 1697, Synopsis). This paper can be regarded as a continuation of the study on that subject first reported in D2 (pages 97 and 98, Introduction).

6.2.1 The authors have discovered that thionyl chloride in pyridine first forms an intermediate compound, which in the presence of an aromatic carboxylic acid is converted into a carboxylic sulfinic anhydride, the latter being reactive enough to selectively activate the carboxylic groups to produce high molecular weight polyesters (D1, page 1698, Results and discussion, mechanism and paragraph 1; D2, page 98, Results and discussion, paragraph 3 and mechanism).

Following the detailed mechanism mentioned in these citations, thionyl chloride first reacts with pyridine to form 1-chlorosulfinyl pyridinium chloride (formulae (I) and (II) in equilibrium), which is then complexed (formula III) with additional pyridine; that intermediate activates the carboxylic acid selectively, whereby a complex ester (formula IV) is obtained in 98% yield; only in the subsequent final step the phenol reacts with that complex ester to give rise to the aromatic ester on alcoholysis (D2, pages 98 to 100, Results and discussion, mechanism; D1, pages 1697 to 1701, Introduction, Results and discussion, mechanism).

Although both articles are basically concerned with the preparation of aromatic polyesters, alternative experiments have also been carried out with other reactants in the final step, namely aniline and aliphatic diols. Whereas benzanilide was obtained in quantitative yield on aminolysis with aniline (D2, page 98, paragraph 3), no polymer was obtained from an aliphatic diol, such as 1,4-cyclohexanediol (D2, page 100, paragraph 2). This raises the question whether, as argued by the appellant, the failure to obtain a high molecular weight polyester from cyclohexanediol should be attributed only to the cyclohexane structure, in other words whether the above polycondensation method would be at all suitable for the preparation of polyesters containing this particular sub-unit.

6.2.2 The above mechanism based on successive complexation, activation and alcoholysis taught in D1 and D2 clearly shows that, when a mixture of carboxylic acid and phenol is added to complex (III), (1) only the carboxylic acid reacts with that complex to form the corresponding carboxylic sulfinic anhydride (IV), and (2) only thereafter the phenol reacts with (IV) to produce the desired ester on alcoholysis. This is confirmed in the passage bridging the pages 1699 and 1700 of D1, wherein it is specified that in the case of dicarboxylic acids and bisphenols the reaction of the complex of thionyl chloride and pyridine with the acid is selective and complete even in the presence of bisphenols.

As the result of their different reactive groups the acid and the phenol are thus involved not only in different reactions, but also in different steps of the above sequence of reactions. Therefore, the fact that an alternative compound, e.g. 1-4-cyclohexanediol, is known to be unsuitable for the final conversion into polyesters does not allow any conclusion about the ability of an acid having the same structure, e.g. cyclohexanedicarboxylic acid, to form the intermediate carboxylic sulfinic anhydride (IV).

6.2.3 Further tests carried out with phenols as well as aniline in the presence of several pyridine derivatives, in particular ∝-, β- and γ-picoline, have demonstrated that β-picoline is effective in ester formation, which is attributed to a higher reactivity of the corresponding intermediate (IV) to nucleophiles (D2, page 99, paragraph 2). More generally, the conversion of the carboxylic sulfinic anhydride into high molecular weight polyesters is said to occur at 80°C only with nucleophiles, e.g. with reactants with sufficient nucleophilicity (D2, page 97, paragraph 3). Thus, an essential feature of the direct polycondensation method as taught in D2 is the nucleophilicity of the phenol.

This explains the different results reported for the alternative experiments with aniline and cyclohexanediol. Whilst aniline as a further nucleophile also tends to give rise to amide formation, aliphatic diols which do not fall into that category do not allow the formation of polymers.

6.2.4 The unsuitability of cyclohexanediol to give rise to polyesters is thus to be attributed to the aliphatic hydroxyl groups, not to the cycloaliphatic structure. Nothing suggests any influence of the latter feature on the polycondensation process, so that in that respect nothing speaks against the use of the thionyl chloride/pyridine system for the preparation by the direct polycondensation method of polyesters derived from cyclohexanedicarboxylic acid.

6.3 The argument presented by the appellant during oral proceedings that the result of the comparative test of example 1 of D5 (column 4, lines 17 to 20), according to which cyclohexanedicarboxylic acid and bisphenol A do not lead to a useful polyester, would discourage a skilled person from considering the direct polycondensation method for the preparation of polyesters derived from that acid, cannot be accepted.

As stated above (points 4.3, 5.1.1 and 5.1.2), D5 is concerned with the preparation of polyesters derived from cyclohexanedicarboxylic acid and aromatic diols by using the transesterification method. In example 1 (column 4, lines 9 to 13) the polyester obtained by using that method is said to have both adequate inherent viscosity and high heat distortion temperature. By contrast, when the direct polycondensation method is used in the absence of any condensing agent, the polymer is not satisfactory (column 4, lines 17 to 20).

This result is not surprising, since the introduction of D1 recalls that the direct polycondensation of dicarboxylic acids and bisphenols requires the use of condensing agents in order to activate the carboxyl groups. Until the studies reported in this citation, which was published more than 20 years after D5, only a limited success could be achieved because the selective activation of carboxyl groups in the mixture is difficult and is usually accompanied by a side reaction of the condensing agents with hydroxyl groups, which has a detrimental effect on the polycondensation process (page 1697, Introduction, paragraph 1).

Thus, the method used in the comparative test in D5 corresponds to an obsolete state of the art and its result would not deter a skilled person from considering an improved direct polycondensation method, e.g. a method based on the use of an efficient condensing agent, for the preparation of polyesters from cyclohexanedicarboxylic acid.

6.4 It follows from these considerations that the direct polycondensation method as disclosed in D1 and D2 would have been regarded by a skilled person as a promising teaching and that, consequently, there was a strong incentive to use it for the preparation of polyesters from cyclohexanedicarboxylic acid and bisphenols. For this reason the claimed subject-matter according to claim 1 must be regarded as obvious and, therefore, as not involving any inventive step.

7. Claim 1 not being allowable, the same applies to dependent process claims 2 to 4 which are directed to preferred embodiments of the process as defined in claim 1 and thus fall with it.

Auxiliary request - Article 123(2) EPC

8. The wording of the claims does not give rise to any objection under Article 123(2) EPC.

8.1 With respect to claim 1 as originally filed the present wording of this claim differs by the specification of the various process steps, namely (i) formation of the condensing agent form thionyl chloride and pyridine, (ii) addition to the condensing agent, in steps, of a cyclohexanedicarboxylic acid and an aromatic diol, and (iii) polycondensation of the resulting mixture to obtain the desired polyester.

The preliminary preparation of the condensing agent (feature (i)) is disclosed on page 8, second paragraph of the application as originally filed. The possibility of the stepwise addition of the reactants (feature (ii)) is mentioned in the sentence bridging pages 8 and 9 of the original application, where it is said that suitably two or three of the raw materials are added sequentially. This embodiment is also illustrated in examples 37 to 46, wherein the different reactants are added in different steps referred to as "first step activation reaction" and "second step activation reaction"; in the particular case of examples 43 and 45 the same reactant (methylhydroquinone respectively chlorohydroquinone) is added portionwise in the two activation steps. As to feature (iii) it must be regarded as a self-evident step in the light of the description (original page 9, lines 3 to 11) and the examples.

Claim 1 as amended is thus adequately supported by the application as originally filed.

8.2 As noted above when discussing feature (ii), the cyclohexanedicarboxylic acid may be added to the condensing agent before the aromatic diol (see in particular examples 37 and 39 to 41), so that claims 2 and 3 are not objectionable.

8.3 The cocondensation of an aromatic hydroxycarboxylic acid with a dicarboxylic acid and an aromatic diol according to claim 4 was the subject-matter of original claim 2; the addition of the aromatic hydroxycarboxylic acid together with the dicarboxylic acid is described in examples 37 and 40. Both features of claim 4 are thus adequately supported.

8.4 Claims 5 and 6 correspond to original claims 3 and 4 with their numbering and appendancies appropriately adjusted.

8.5 The addition of the reactants over a period of five minutes to two hours according to claim 7 is disclosed in the sentence bridging pages 8 and 9 of the original application.

Inventive step

9. The properties of the polyesters obtained in the application in suit by the stepwise activation reaction, e.g. by following the procedure described in examples 37 to 46, do not show any improvement either in terms of inherent viscosity or in terms of melting point. Whether one considers the properties achieved in the other examples of the application or those reported in D3 (column 7, lines 32 to 37: inherent viscosity up to 9.0 dl/g; column 3, lines 13 to 16: melting temperature of at least 235°C as determined by

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differential scanning calorimetry), wherein in both cases the various reactants are wholly present at the beginning of the reaction, it is evident that the particular method of adding the reactants according to the auxiliary request has no effect on the properties of the polyesters, at least on those considered in the application.

Thus in this case too, the technical problem can be defined only in alternative terms, namely the provision of a further process for producing known polyesters.

10. As stated above (cf. points 6.2.1 and 6.2.2), the mechanism explained in D1 and D2 relies on successive complexation, activation and alcoholysis reactions. A major discovery by the authors is that, when thionyl chloride in pyridine is treated with a mixture of carboxylic acid and phenol, the acid is selectively activated to give the benzoate in 98% yield (D1, page 1698, paragraph 1). This selective and complete activation has the advantage that polyesters of high molecular weight can be produced without initial activation of the dicarboxylic acids by simply adding the acid and the phenol simultaneously; the results are said to be almost comparable to those obtained by initial activation of the acids followed by alcoholysis with bisphenols (paragraph bridging pages 1698 and 1699).

Thus, whether one has a stepwise addition of the reactants, as required in the auxiliary request, or a simulaneous addition has no influence on the actual sequence of reactions, which is always an activation of the carboxylic acid followed by alcoholysis, nor in effect on the properties of the final product. The skilled person would thus have been well aware of these two alternative embodiments of the direct polycondensation method as taught in D1; in the absence of any technical effect the selection of the one based on the stepwise activation/reaction cannot be regarded as inventive.

11. Claim 1 not being allowable, the same applies to dependent process claims 2 to 7 which are directed to preferred embodiments of the process as defined in claim 1 and thus fall with it.

Order

For these reasons it is decided that:

The appeal is dismissed.

The Registrar:

E. Görgmaier

The Chairman:

C. Gérardin

C. Gérardin