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DECISION
of 29 September 2000

Case Number: T 0063/98 - 3.3.3

Application Number: 93117150.8

Publication Number: 0594191

IPC: C08G 75/02

Language of the proceedings: EN

Title of invention:
Process for the removal of lower molecular weight fractions of poly(arylene sulfide) polymers

Applicant:
PHILLIPS PETROLEUM COMPANY

Opponent:
-

Headword:
-

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step - non-obvious improvement"

Decisions cited:
-

Catchword:
-

Case Number: T 0063/98 - 3.3.3

DECISION
of the Technical Board of Appeal 3.3.3
of 29 September 2000

Appellant:

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Decision under appeal:

Decision of the Examining Division of the European Patent Office posted 1 August 1997 refusing European patent application No. 93 117 150.8 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: C. Gérardin
Members: P. Kitzmantel
V. Di Cerbo

Summary of Facts and Submissions

I. This appeal, which was filed on 8 October 1997, lies against the decision of the Examining Division dated 1 August 1997, refusing European patent application No. 93 117 150.8 filed on 22 October 1993 in the name of PHILLIPS PETROLEUM COMPANY, and published under No. 0 594 191. The appeal fee was paid together with the Notice of Appeal and the Statement of Grounds of Appeal was filed on 11 December 1997.

II. The decision under appeal was based on a main request and on a first auxiliary request, both filed with a submission dated 10 June 1997, as well as on a second, third and fourth auxiliary request, all filed on 10 July 1997 during oral proceedings before the Examining Division.

(i) Claim 1 of the main request read as follows:

"1. A method for selectively removing a low molecular weight portion from an arylene sulfide polymer which comprises:

a) contacting said polymer with a polar organic compound being a solvent for the polymer and a promoter selected from water, an alkali metal salt and mixtures thereof, wherein said promoter is soluble in said polar organic compound, to form a less dense polymer-lean liquid phase and a more dense polymer-rich liquid phase, and wherein the majority of the insoluble alkali metal halide formed as a by-product of the poly(arylene sulfide) polymerization has been removed prior to said contacting;

b) separating and thus removing said polymer-lean phase from said polymer-rich phase; and

c) recovering the low molecular weight portion-depleted arylene sulfide polymer from said polymer-rich phase."

Claims 2 to 8 of the main request were dependent on Claim 1.

Independent Claim 9 of the main request related to a method for selectively producing an arylene sulfide polymer having a desired molecular weight distribution comprising step (a) according to Claim 1 and the following steps (b), (c) and (d):

"b) separating the polymer-lean phase from the polymer-rich phase;

c) repeating steps (a) and (b) one or more times using the polymer-lean liquid phase produced in step (a), or the polymer-rich liquid phase produced in step (a), or each of said phases separately; and

d) recovering said arylene sulfide polymer having a desired molecular weight distribution from said phase or phases employed in step (c)."

(ii) The first auxiliary request differed from the main request by amendment in paragraph (a) of

Claims 1 and 9 of the statement: "... and a promoter selected from water, an alkali metal salt and mixtures thereof, ..." to "... and a promoter selected from water and mixtures thereof with an alkali metal salt, ...".

(iii) The second auxiliary request differed from the first auxiliary request by insertion in paragraphs (a) and (b) of Claims 1 and 9 of the passages hereinafter printed in **bold**:

- paragraph (a) of Claims 1 and 9: "... and a promoter selected from water **in an amount necessary to aid in the formation of two phases** and mixtures thereof with an alkali metal salt, ...";

- paragraph (b) of Claim 9: "separating the polymer-lean **liquid** phase from the polymer-rich **liquid** phase;"

(iv) The third auxiliary request differed from the first auxiliary request by the same amendment of paragraph (a) of Claims 1 and 9 as according to the second auxiliary request and by the insertion in paragraphs (b) of Claims 1 and 9 of the terminal statement hereinafter printed in **bold**:

- paragraph (b): "... polymer-rich phase **at a temperature of 200°C to 300°C**;"

(v) The fourth auxiliary request differed from the third auxiliary request only with regard to the narrower temperature range of from "220°C to

280°C" in paragraph (b) of Claims 1 and 9.

III. The decision under appeal refused the application because, in the Examining Division's opinion,

- Claims 1 and 9 of the third and fourth auxiliary requests did not comply with the requirement of Article 123(2) EPC,

- Claim 1 of the main and first auxiliary request did not comply with the requirement of Article 84 EPC in that an essential feature concerning the separation of the two phases while in liquid phase was missing,

- the subject-matter of Claim 1 of the main request and of the first auxiliary request did not comply with the requirement of Article 54 EPC, and

- the subject-matter of Claims 1 and 9 of the second auxiliary request did not comply with the requirement of Article 56 EPC.

The novelty objection against the subject-matter of Claim 1 of the main and first auxiliary requests was based on the disclosure of document

D4: US-A-4 748 231,

according to which raw poly(arylene sulfide) (hereinafter PAS) was purified from low molecular weight portions by (i) dissolving it in a mixture of polar organic solvent, alkali metal carboxylate and water, (ii) addition of water to cause formation of a two-phase system, (iii) cooling thereof until solidification of the polymer-rich phase and (iv) recovery of the latter.

While, in the Examining Division's view, the feature in Claims 1 and 9 of the second auxiliary request that the polymer-lean and the polymer-rich phases are liquid would establish novelty over D4, it was not able to provide an inventive step, because liquid-liquid phase separation of polymers was an obvious alternative to the liquid-solid separation used according to D4; on the one hand, according to

F. W. Billmeyer, "Textbook of Polymer Chemistry", 3rd ed., 1984, pages 177 to 179, hereinafter D6,

this technique was standard in polymer chemistry, and on the other hand it was even known from document

D1: DE-A-3 527 492

to be applicable to PAS.

IV. Together with the Statement of Grounds of Appeal filed on 11 December 1997 the Appellant submitted an amended set of claims, which was further amended, in response to the Board's first communication dated 1 February 2000, with a reply dated 29 May 2000. In view of the latter, the holding of oral proceedings, originally requested by the Appellant, became unnecessary. After the Board's second communication of 27 July 2000 the final set of Claims 1 to 9 was filed with the Appellant's submission dated 25 September 2000.

Independent Claims 1 and 9 of this set read as follows:

"1. A method for selectively removing a low molecular weight portion from an arylene sulfide polymer by a liquid-liquid phase separation which comprises:

a. contacting said polymer with a polar organic compound being a solvent for the polymer and a promoter selected from the group consisting of an alkali metal halide which is soluble in said polar organic compound, an alkali metal carboxylate, water, and mixtures thereof, to form a less dense polymer-lean liquid phase and a more dense polymer-rich liquid phase, and wherein the majority of the insoluble alkali metal halide formed as a by-product of the poly(arylene sulfide) polymerization has been removed prior to said contacting;

b. separating and thus removing said polymer-lean liquid phase from said polymer-rich liquid phase; and

c. recovering the low molecular weight portion-depleted arylene sulfide polymer from said polymer-rich phase."

"9. A method for selectively producing an arylene sulfide polymer having a desired molecular weight distribution, which method comprises:

a. contacting said polymer with a polar organic compound being a solvent for the polymer and a promoter selected from the group consisting of an alkali metal halide which is soluble in said polar organic compound, an alkali metal carboxylate, water, and mixtures thereof, to form a less dense polymer-lean liquid phase and a more dense polymer-rich liquid phase, and wherein the majority of the insoluble alkali metal halide formed as a by-product of the poly(arylene sulfide) polymerization has been removed prior to said contacting;

b. separating the polymer-lean liquid phase from the polymer-rich liquid phase;

c. repeating steps (a) and (b) one or more times using the polymer-lean liquid phase produced in step (a), or the polymer-rich liquid phase produced in step (a), or each of said phases separately; and

d. recovering said arylene sulfide polymer having a desired molecular weight distribution from said phase or phases employed in step (c)."

Dependent Claims 2 to 8 relate to preferred embodiments of the subject-matter of Claim 1.

V. The Appellant essentially argued that the above wording of the independent claims overcame the previous objections under Article 84 EPC and that the claimed subject-matter was novel and inventive

(i) over D4, because this document only related to solid-liquid, not to liquid-liquid phase separation, and did not contain any suggestion of the latter technique,

(ii) over D6, which disclosed different, industrially not applicable liquid-liquid phase separation methods and

(iii) also over D1, which related to a liquid-liquid phase separation method, wherein insoluble metal halide was not removed prior to the phase separation process, prohibiting thereby an efficient purification of the high molecular weight PAS-portion from low molecular weight by-product, as evidenced by Example X of the application in suit and confirmed by the Declaration of Mr. Jon. F. Geibel attached to the Appellant's submission dated 29 May 2000.

VI. The Appellant requested that the decision under appeal be set aside and a patent be granted on the basis of the following version:

Claims:	1 to 9 filed with the submission dated 25 September 2000,
Description:	pages 1 to 29 filed with the submission dated 25 September 2000, and
Figures:	1 to 10 as originally filed.

Reasons for the Decision

1. The appeal is admissible.

2. *Amendments (Article 123(2) EPC)*

From Claim 1 as originally filed operative Claim 1 is different by the following insertions printed in bold:

(i) "A method for selectively removing ... **by a liquid-liquid phase separation** ..."

(ii) "a) contacting said polymer with a polar organic compound **being a solvent for the polymer** ..."

(iii) "a) ... and a promotor **selected from from the group consisting of an alkali metal halide which is soluble in said polar organic compound, an alkali metal carboxylate, water, and mixtures thereof,**...."

(iv) "..., **and wherein the majority of the insoluble alkali metal halide formed as a by-product of the poly(arylene sulfide) polymerization has been removed prior to said contacting;** ..."

(v) "b) separating ... said polymer-lean **liquid** phase from said polymer-rich **liquid** phase; ..."

The amendments (i) and (v) are based on page 11, lines 3 to 14, amendment (ii) on page 7, lines 23 to 25, amendment (iii) on page 2, lines 15 to 19 and amendment (iv) on page 10, lines 16 to 21 of the application as filed.

The amendments of Claim 9 correspond to those in Claim 1, Claims 2 to 8 are identical to the same claims of the application as filed.

The requirement of Article 123(2) EPC is therefore complied with by all claims.

3. *Article 84 EPC*

These amendments also satisfy the requirements of Article 84 EPC. First, the indication that the low molecular weight fraction is removed by a liquid-liquid phase separation results in a definition of the method which is now in line with the essential features of the description. Secondly, the distinction between the soluble alkali metal halide promotor and the insoluble alkali metal halide by-product avoids any inconsistency in the description of step a.

4. *State of the art*

4.1 Document D1

Claim 1 of this document relates to a process for the preparation of PAS comprising reacting a polyhalogenated aromatic compound and a sulphidising agent in a polar amide solvent and in the presence of at least one polymerisation additive (e.g. metal salts of organic sulfonic acids and carboxylic acids, lithium halogenides, alkali salts of phosphoric acid: page 12, lines 27 to 30) in such a manner that a resin liquid comprising two layers is formed, namely a layer (I) comprising a major amount of a polymer having a relatively high molecular weight and a small amount of a polymer having a relatively low molecular weight, and a layer (II) comprising a major amount of a polymer having a relatively low molecular weight and a small amount of a polymer having a relatively high molecular weight, and fractionating one of the layers (I) or (II) from the resin liquid.

The presence of a polymerisation additive is said to be necessary in order to achieve the desired phase separation (page 16, lines 24 to 32; pages 40 to 41, Comparative Example and Table 8).

4.2 Document D4

Claim 1 of this document relates to a method for increasing the molecular weight of linear PAS comprising (a) heating a mixture comprising linear PAS, polar organic solvent, and alkali metal carboxylate, with or without water, to at least the dispersion temperature of said linear PAS in said solvent, (b) maintaining said mixture at said dispersion temperature for a sufficient length of time in order to achieve dispersion, (c) adding sufficient water to cause phase separation, (d) slowly cooling said mixture and water to at least about 200°C, and (e) recovering a linear PAS of increased molecular weight from said mixture.

The recovering is accomplished by separation of the granular PAS, which precipitates on cooling, by filtration (column 2, lines 9 to 26; column 7, lines 39 to 41; Examples I to V).

4.3 Document D6

This textbook citation relates to two methods for the "Fractionation of Polymers by Solubility"; namely, either by repeated addition of nonsolvent to a dilute solution of the polymer (page 177, Section "Bulk Fractionation by Nonsolvent Addition") or by elution of polymer fractions from a column with a series of liquids of gradually increasing solvent power such that the species of lowest molecular weight and highest solublity are dissolved first (page 177, Section

"Column Elution", Sub-section "Solvent-Gradient Elution").

5. *Novelty (Article 54 EPC)*

The subject-matter of independent Claims 1 and 9 is novel over the cited prior art.

Novelty over D1 is established by the feature of the removal from the starting PAS of the majority of the insoluble alkali metal halide formed as a by-product of the polymerization.

Novelty over D4 is established by the restriction to the technique of liquid-liquid phase separation.

6. *Problem and solution*

6.1 Closest prior art

In view of the fact that both D1 and the application in suit are concerned with the separation of raw PAS into high and low molecular weight fractions by liquid-liquid phase separation, D1 is to be regarded as representing the closest prior art (cf. point 3.1 supra).

Document D4 is a much less appropriate starting point, because (i) it is mainly concerned with a method for increasing the molecular weight of PAS, (ii) separates the precipitated PAS from the liquid reaction mixture by filtering and (iii) is silent about the separation of any low molecular weight fractions (cf. point 3.2 supra).

6.2 Problem to be solved

The problem underlying the claimed subject-matter with respect to D1 is the provision of a method of liquid-liquid phase fractionation of PAS, which allows an improved separation of high molecular weight fractions and low molecular weight (i.e. oligomer) fractions.

6.3 Solution of the problem

According to Claim 1 this problem is to be solved by the removal from the starting PAS of the majority of the insoluble alkali metal halide formed as a by-product of the polymerization.

On the basis of the evidence contained in the Declaration of Mr Geibel (cf. point V (iii) supra) the Board is satisfied that this problem has effectively been solved by that measure.

This Declaration compares the efficiency of the removal of low molecular weight oligomer fractions from PPS (polyphenylene sulphide) solutions in the presence and absence of sodium chloride. The data show that in the absence of sodium chloride the GPC (gel permeation chromatogaraphy) peak molecular weight of the two fractions is considerably different (cf. Figure 5), whereas in the presence of sodium chloride there is hardly any difference in the GPC molecular weights of the two fractions.

The Board is satisfied that these effects can essentially be attributed to the presence or absence of sodium chloride; the different molecular weights of the PPS polymers used (PPS free of sodium chloride: melt flow 248 g/10 min; PPS with sodium chloride: melt flow 348 g/10 min: page 2 of Declaration, points 4 and 5), should not affect this conclusion, because there is no reason to assume that this difference has any substantial impact on the separation characteristics.

7. *Obviousness*

This issue turns on the question whether, for the skilled person looking for a solution of the existing technical problem (cf. 5.2 supra), there was any clue in the prior art towards the subject-matter of present Claim 1.

The following considerations lead to the conclusion that this is not the case, i.e. that the claimed subject-matter is inventive over the citations on file.

7.1 According to D1, without removal from the reaction mixture of the by-product sodium chloride, a solution of PAS, resulting from the reaction of polyhalogenated aromatic compounds and sulphidizing agent in a polar amide solvent, separates into two layers comprising fractions of different molecular weight, if the solution contains a polymerisation additive, e.g. sodium p-toluene sulphonate (D1: pages 24 to 27, Example 1, Table 1; page 40, Comparative Example; point 3.1 supra).

Not only is there no suggestion in D1 of the possible removal of sodium chloride prior to the liquid-liquid phase separation step, but D1 may even be considered to militate against this measure, because the removal of sodium chloride goes against an essential aspect of the teaching of D1, namely avoiding a separate step for the extraction of low molecular weight fractions from a prefabricated PAS, as was necessary in prior art methods, such as known from US-A-3 607 843 (cf. page 6, lines 11 to 27 of D1).

7.2 Since D4 makes no use of the liquid-liquid phase separation of PAS solutions, it cannot suggest the importance of the removal of sodium chloride for this technique (cf. point 4.2 supra).

7.3 Document D6 is of no relevance for the issue of obviousness of the present subject-matter, because it does not refer to liquid-liquid phase separation, but to the isolation of polymer fractions according to their solubility/molecular weight by solvent elution from a column or to fractional precipitation of polymer species by addition of a non-solvent to a dilute solution of the polymer (cf. point 3.3 supra).

7.4 The subject-matter of Claim 1 is, thus, not obvious over either of the citations and, therefore, involves an inventive step.

7.5 The same conclusions are *a fortiori* to be drawn with respect to the subject-matter of independent Claim 9, which applies the liquid-liquid phase separation technique according to Claim 1 to a method for selectively producing a PAS having a desired molecular weight distribution, and with respect to the subject-matter of dependent on Claims 2 to 8.

8. Since the operative claims satisfy all the requirements of the EPC and the description has been adapted to them, there is no obstacle to the grant of the patent.

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 the version set out in point VI supra.

The Registrar:	The Chairman:
E. Görgmaier	C. Gérardin