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Aktenzeichen / Case Number / N^o du recours : T 172/85 - 3.3.1

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Veröffentlichungs-Nr. / Publication No / N^o de la publication : 0 008 894

Bezeichnung der Erfindung: Sulphonated polyarylethersulphone copolymers and
Title of invention: process for the manufacture thereof
Titre de l'invention :

Klassifikation / Classification / Classement : C08G 75/23

ENTSCHEIDUNG / DECISION

vom / of / du 19 April 1988

Anmelder / Applicant / Demandeur :

Patentinhaber / Proprietor of the patent /
Titulaire du brevet :

ICI PLC

Einsprechender / Opponent / Opposant :

Rhône-Poulenc Spécialités Chimiques

Stichwort / Headword / Référence :

EPÜ / EPC / CBE Article 56

Kennwort / Keyword / Mot clé : "Inventive step - selection"

Leitsatz / Headnote / Sommaire

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European Patent
Office
Boards of Appeal

Office européen
des brevets
Chambres de recours



Case Number : T 172/85 - 3.3.1

D E C I S I O N
of the Technical Board of Appeal 3.3.1
of 19 April 1988

Appellant :
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Decision under appeal : Decision of the Opposition Division of the European Patent Office dated 9 May 1985 rejecting the opposition filed against European patent No. 0 008 894 pursuant to Article 102(2) EPC.

Composition of the Board :

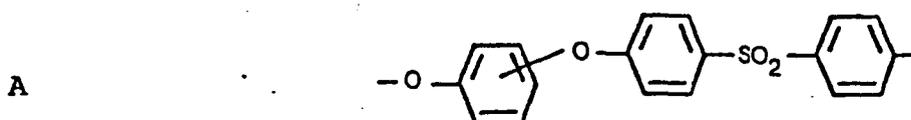
Chairman : K. Jahn
Members : C. Gérardin
P. Ford

Summary of Facts and Submissions

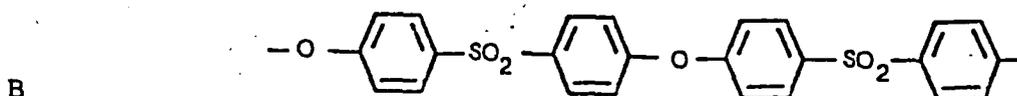
- I. The mention of the grant of the patent No. 8894 in respect of European patent application No. 79 301 674.2 filed on 16 August 1979 and claiming priorities of 5 September 1978 and 24 January 1979 from two earlier applications GB-3 558 978 and GB-7 902 490 was announced on 23 February 1983 on the basis of seven claims.

Claim 1 reads as follows:

"A polyarylethersulphone copolymer which is a hydrophilic sulphonated copolymer derived by controllably sulphonating a copolymer having the repeat unit of formula



together with the repeat unit of formula



substantially all the sub-units



in said units A being sulphonated after sulphonation and substantially all the units B remaining non-sulphonated after sulphonation".

II. The Appellant (Opponent) filed an opposition against the grant of the patent on 18 November 1983 on grounds of lack of novelty and inventive step. The following documents were cited in support of the opposition:

- (1) US-A-3 709 841
- (2) FR-A-1 407 301
- (4) US-A-4 054 707.

Besides this ground of opposition under Article 100(a) EPC, the Opponent put forward on 17 September 1984 that the disputed patent did not disclose the preparation of the copolymers used in the examples 1 to 6 in a manner sufficiently clear and complete for it to be carried out by a person skilled in the art (Article 100(b) EPC).

III. The Opposition Division rejected the opposition in a decision dated on 9 May 1985 based on the following arguments:

Novelty: the sulphonated polyarylethersulphones of formula (I) disclosed in document (1) are prepared by sulphonation of polymers of formula (II) which are themselves described in document (2). Although the latter document mentions in general terms the possibility of using mixtures of reactants, the word "copolymer" appears nowhere and only a mixture of isomeric diphenols is actually used in one example. The specific polysulphone copolymers of formula (II) which, upon sulphonation as disclosed in document (1), will give rise to the claimed polymers, cannot thus be regarded either implicitly or explicitly as described in document (2).

Inventive step: nothing in document (1), read together with document (2), would suggest the particular copolymer according to Claim 1 of the disputed patent since this

combination of recurrent units can only result from experimental conditions which do not correspond to the prior teachings. Whereas document (1) suggests to adjust the sulphonation conditions, the present invention relies on a selective reactivity to sulphonation of different recurrent units.

Insufficient disclosure: as far as the preparation of copolymers is concerned, the disputed patent refers to CA-A-847 963, which discloses that the polycondensation of the appropriate reactants is suitably carried out in the presence of an alkali metal carbonate or bicarbonate and of a sulphone or sulfoxide solvent. The present invention only requires a simple alteration of this method in order to take the presence of a mixture of two specific diphenols into account, which certainly is within the realm of the skilled man. Moreover, a contradiction is seen between this objection under Article 100(b) and the previous objection raised under Article 100(a), which is based on the obviousness of copolymers once the homopolymers are known.

- IV. The Appellant thereafter filed a notice of appeal on 29 June 1985 and paid the prescribed fee at the same time. The arguments presented in the Statement of Grounds filed on 1 August 1985 and in the subsequent statement referred to additional documents, FR-A-1 321 798 (document (3)) and FR-A-1 361 067 (document (5)); they only concerned the objection of lack of inventive step and can be summarised as follows:

It is generally known from document (1) that sulphonated polyarylethersulphones are particularly suitable for the manufacture of membranes useful in ultrafiltration and that these polymers can be obtained by sulphonation with sulphuric acid of the corresponding non-sulphonated polysulphone. This reaction is even the major teaching of documents (3) and (5), which specify that copolymers with

benzene rings can be suitably sulphonated with sulphuric acid.

The recurrent units A and B of the copolymers according to the disputed patent are each known from one example of document (2); since this document mentions the possibility of using mixtures of diphenols, it is clear that copolymers are within the scope of this document as well. All the Respondent had to do was thus to try to sulphonate the polysulphones exemplified in document (2) and, having noticed the different reactivities to sulphonation with sulphuric acid of the polysulphones according to examples 6 and 13, to combine both recurrent units into a copolymer.

As far as the properties of the copolymers according to the patent-in-suit are concerned, they are not surprising at all since their applications correspond to those of the polymers described in document (1).

- V. In the statement of rebuttal of 6 December 1985 and subsequent statements the Respondent put forward essentially the following arguments:

Document (3) is concerned with polymer structures wherein the benzene rings do not form part of the polymer main chain, but are pendant groups attached to this backbone; as to document (5), it would rather suggest the use of chlorosulphonic acid as sulphonating agent which would reinforce the prejudice against using sulphuric acid.

In respect of the mention in document (1) of the use of sulphuric acid as a sulphonating agent, evidence has been provided in opposition procedure that sulphonation of the only polymer actually exemplified in this document with sulphuric acid results in a water-soluble product totally unsuitable for the production of membranes for use in an aqueous medium.

In the general formula (I) of the sulphonated polymers described in document (1), the integer m has a value 0 or 1. Polymers where m is both 0 and 1 in a single chain, like in the disputed patent, cannot be suggested by the teaching of document (1) since they would be outside the scope of this disclosure.

Document (2) is, in fact, a very broad disclosure which may include as starting compounds different diphenols as well as different dihalobenzenoid compounds; the many possibilities encompassed give no direction to the specific combination required in accordance with the patent-in-suit.

The documents relied upon do not suggest that the polymers will behave differently under sulphonation conditions and that this selective reactivity could be used to determine the extent of sulphonation of the copolymer.

- VI. In a communication the Board noted that all the arguments presented by the Patentee (Respondent) in opposition procedure as well as in the appeal stage concerned the preparation of the copolymers and that the file did not contain any evidence demonstrating superior properties of the copolymers due to the particular distribution of the sulphonic groups along the polymer backbone.

During oral proceedings held on 19 April 1988 the properties of the copolymers according to the patent-in-suit, especially the burst strength and the glass transition temperature, were discussed in the light of the comparative tests provided by the Respondent on 21 March 1988. The Appellant argued against the inventiveness of the products on the basis of five new documents disclosing similar properties for other polymers.

VII. The Appellant requests the impugned decision be set aside and the patent revoked in its entirety. The Respondent requests 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. As already specified in the unpublished Decision of the Technical Boards of Appeal T 49/85 of 13 November 1986, a document filed for the first time by an Opponent with his Statement of Grounds for the appeal is considered as not submitted in due time under Article 114(2) EPC unless representing the effective counter-evidence to a newly emphasised reason given in the decision. However, it is within the discretion of the Board under Article 114(1) EPC to admit and consider such a document in the proceedings in view of its relevance (point 2).

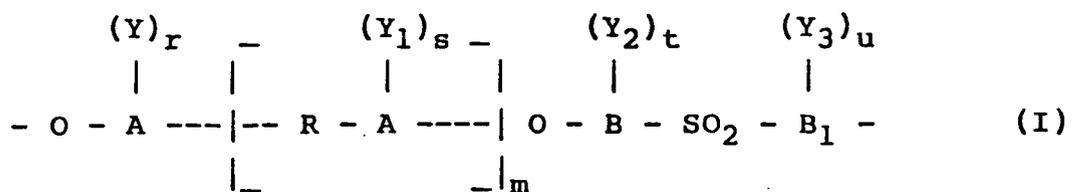
In the present case, the degree of relevance of documents (3), (5) and of the five documents submitted in oral proceedings is considered to be minimal. The sulphonated copolymers disclosed in document (3) are obtained by addition copolymerisation of at least one aromatic vinyl hydrocarbon and at least one polyunsaturated vinyl monomer acting as cross-linking agent in presence of minor amounts of a polymerisable polar compound (page 1, column 2, paragraph 3 to page 2, column 1, line 6), followed by sulphonation with sulphuric acid (page 1, column 1, line 7; examples 1 to 7, 11, 13 and 16). In the resulting copolymer, the benzene rings do not form part of the main polymer chain, but are pendant groups attached to this backbone. As to document (5), it concerns the sulphonation of polyphenylene ether polymers (PPO) with a sulphonating agent which can be sulphuric acid although it

is not exemplified. The properties of the resulting polymers are actually controlled by the radicals on the aromatic rings and by the amount of sulphonic groups, the latter feature suggesting a partial sulphonation (page 1, column 2, paragraph 5 to page 2, column 1, paragraph 1). These two documents, therefore, are not considered to add anything of substance to the content of documents (1) and (2).

The documents submitted in oral proceedings represent a survey of the properties of sulphonated aromatic polysulphones derived from bis-phenol A and dichlorodiphenylsulphone (Udel polysulphones) which are the polymers disclosed in document (1) as well as of the properties of the membranes made therefrom. The mere fact that some of these properties may appear comparable with those of the copolymers with hydroquinone sub-units cannot lead by itself to the subject-matter of the patent-in-suit.

For all these reasons, the content of the late filed documents will be disregarded hereinafter.

3. The patent relates to sulphonated polyarylethersulphone copolymers and to a process for the manufacture thereof. In the Board's view, the closest state of the art is represented by document (1) which describes cation exchange resins with the following recurrent units:



in which

A, B and B₁, which may be identical or different, represent aromatic radicals of which at least one is substituted by a sulphonic radical,

Y and Y₁, which may be identical or different, represent substituent radicals which are inert to sulphonation,

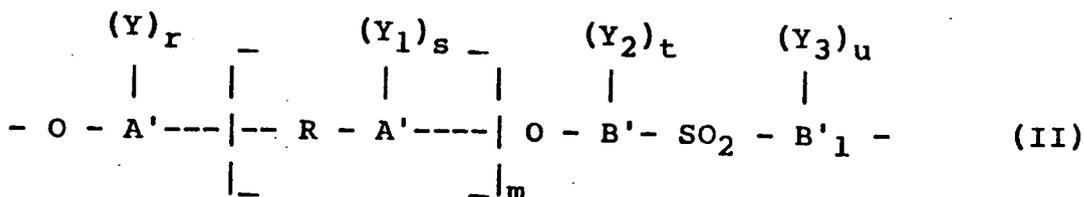
Y₂ and Y₃, which may be identical or different, represent electron acceptor radicals,

r, s, t and u, which may be identical or different, represent integers of 0 to 4 inclusive, at least one of them being less than 4,

m is 0 or 1, and

R represents a valency bond, - CO -, - O -, - SO₂ - or a divalent organic hydrocarbon radical (column 1, lines 37 to 53).

These ion exchange resins are obtained by sulphonating polyarylethersulphones having following recurrent units



in which A', B' and B'₁, which may be identical or different, represent aromatic radicals, at least one of them differing from its counterpart in formula I by not containing a sulphonic radical (column 2, lines 3 to 17).

Formulae (I) and (II) show that sulphonation may occur on any of the aromatic radicals A, B and B₁, which means that the sulphonic radicals are distributed all along the polymer chain; in this regard, no difference is made between phenylene, diphenylsulphone or any A'-R-A' radical in their reactivity to the sulphonating agent. As to the starting diphenol, it has either the formula HO - A' - OH

corresponding to $m = 0$, or the formula $\text{HO} - \text{A}' - \text{R} - \text{A}' - \text{OH}$ corresponding to $m = 1$; mixtures of both leading thus to copolymers are not disclosed.

It is specified (column 2, lines 21 to 23) that the starting polyarylethersulphones of formula II are described in document (2). This document, which is not concerned with sulphonation of polymers at all, teaches the preparation of polyarylene ethers of high molecular weight; when 4,4'-dichlorodiphenylsulphone is used for the polycondensation, the resulting polymer contains sulphone linkages and falls thus within formula II (examples 1 to 10, 13, 14 and 16). All such polymers are thus obtained from one single diphenol in contrast to the patent-in-suit where the polycondensate requires a mixture of two specific diphenols.

According to document (1) many sulphonation reagents, including sulphuric acid, are suitable for the reaction with the polymers of formula (II) (column 2, lines 24 to 30); in practice, however, sulphonation is carried out with chlorosulphonic acid (examples 1 to 4, 6, 8 to 10) and sulphur trioxide (examples 5 and 7) which are mentioned as the preferred reagents. Regardless of the process by which the polyarylethersulphones are sulphonated, the amount of sulphonic acid groups attached is controlled by adjusting the sulphonation conditions, in particular the temperature, the duration of the reaction and the concentration of the reagents (column 2, lines 44 to 49).

Although the membranes made from these polymers exhibit satisfactory ion exchange capacities, some of their physical properties, especially the glass transition temperature and the burst strength, did not meet the requirements compatible with the use thereof in the field of reverse osmosis or gas separation. As to the process of

preparation of the polymers of formula (I), its sensitivity to so many reaction parameters made it somewhat cumbersome.

4. In the light of this closest prior art, the technical problem underlying the patent-in-suit can be seen in providing sulphonated polyarylethersulphones with the above mentioned improved physical properties as well as a process for the preparation thereof which is free from any particular adjustment of the sulphonation conditions.

This problem is solved according to the patent-in-suit by providing as polymer to be sulphonated, a copolymer as specified in Claim 1, i.e. essentially obtained from two different diphenols (see patent description, page 3, lines 18 to 22), one being highly reactive to sulphuric acid used as sulphonating agent, the other being virtually inert under the same conditions. This results in a sulphonated copolymer wherein the sulphonic radicals are attached on specific nuclei only.

In view of the results obtained in the Examples of the patent-in-suit and the above mentioned comparative tests provided by the Respondent, the Board is satisfied that this technical problem has been plausibly solved.

5. The solution claimed by the Respondent is not to be found in any prior document so that novelty is acknowledged. Since novelty is no longer questioned by the Appellant, further considerations in this respect are superfluous.

It has thus to be examined whether the subject-matter of the patent-in-suit involves an inventive step.

6. The prior art teaches that the sulphonic groups may be distributed on any aromatic ring along the polymer backbone.

- 6.1 According to formula (I) in document (1) the sulphonic groups in the sulphonated polyarylethersulphones are distributed on the two aromatic rings B and B₁ of the diphenylsulphone radical as well as on the aromatic ring(s) A of the diphenol radical. No difference is thus made as to the sulphonation rate on the aromatic ring(s) A when m is 0, i.e. when the diphenol used is hydroquinone or resorcinol, and when m is 1, i.e. when the diphenol contain two rings separated by a linkage R, which means that the structure of the diphenol is not considered essential for its reactivity to the sulphonating agent as long as the possible substituents Y and Y₁ are inert to sulphonation. As to the distribution of the sulphonic groups, it may or may not be uniform between the rings A, B and B₁ and any ring might be more sulphonated than the other two. However, these possible differences do not suggest the presence of units totally inert to sulphonation and cannot be regarded as the result of the choice of certain diphenols according to criteria of reactivity to sulphonating agents, let alone to the non-preferred sulphuric acid.
- 6.2 A similar teaching is to be found in document (4), which aims at the manufacture of membranes with improved properties with regard to those known from document (1) (column 1, lines 8 to 52). This improvement is achieved by condensing specific diphenols with 4,4'-dichlorodiphenylsulphone and by sulphonating the resulting polyarylethersulphone under the sulphonation conditions already described in document (1), i.e. by adjusting the temperature and the duration of the reaction as well as the concentration of the reagents (column 2, lines 17 to 22). The sulphonated polymers contain five aromatic rings A₁ to A₅ per recurrent unit (I), at least one of them being substituted by a sulphonic group, and are therefore structurally far remote from the polymers according to the patent in suit. Although different sulphonation rates are envisaged for the various aromatic rings, this does not

teach a selectivity of this reaction on certain rings only, as suggested by the invention.

- 6.3 Documents (1) and (4) are thus based on the same concept in that sense that they do not suggest a possible correlation between recurrent units and reactivity to a given sulphonation reagent, nor give the least information regarding the influence of specific recurrent units on the above mentioned physical properties of the copolymers, envisaged by the patent in suit.

7. Interpretation of document (1) in the light of the teaching of document (2) cannot lead the skilled man to a copolymer based on a specific combination of diphenols.

Document (2) contains no specific example of copolyarylethersulphones and the description mentions only in general terms the possibility of using two or more diphenols (page 5, column 1, lines 16 to 18) as well as any mixture of dihalogenated aromatic compounds (page 5, column 1, lines 30 to 32). The isomeric mixture of diphenols used according to example 12 can hardly be considered as a mixture of different diphenols within the meaning of the patent-in-suit, all the more as it is reacted with a benzophenone, not with a diphenylsulphone, leading thus to a polyetherketone, not to a polyethersulphone.

The essential statement in document (2) concerning the selection of the diphenol is that the structure of the diphenol is not important as such, even if the choice of this compound may affect the kinetics and the yield of the reaction, the optimal reaction temperature for the preparation of the polymer as well as certain properties of the polymer (page 3, column 2, paragraph 5 and page 5, column 1, lines 4 to 15). In this regard, the diphenol can be mononuclear, such as hydroquinone or resorcinol (page 3, column 2, paragraph 4), or preferably it can contain two

rings which may be separated by a sulphone linkage (page 4, column 2, paragraph 3 to page 5, column 1, line 1, especially formula (b)). In fact, in view of the high molecular weight to be achieved (page 1, column 1, lines 6 to 12), the choice of the diphenol is mainly dictated by its reactivity with the dihalogenated compound which makes dinuclear diphenols with a strong activating group between the two benzenoid rings particularly appropriate (page 3, column 2, paragraph 5 to page 4, column 1, paragraph 1).

Thus, even if the skilled man had been tempted to use a mixture of diphenols, high reactivity with dihalogenated compounds would have been the first criterion for his choice, not selective reactivity to a specific sulphonating reagent; this simple condition already leads away from any combination involving the mononuclear diphenol used in example 6.

8. Several reagents are convenient to carry out the sulphonation of the polymers of formula (II) in document (1): chlorosulphonic acid, sulphur trioxide, addition products of sulphur trioxide with Lewis bases containing oxygen as an electron donor atom, sulphuric acid and oleum; the first two are preferred and actually used in all the examples (column 2, lines 24 to 30). This teaching is confirmed in document (4) which specifies that chlorosulphonic acid is the preferred sulphonating agent and that sulphuric acid among others can be used as well (column 1, line 64 to column 2, line 5; Example).

The comparative test provided by the Respondent on 16 April 1984 in opposition procedure which shows that sulphuric acid would not be suitable to sulphonate a polyarylethersulphone polymer obtained from dichlorodiphenylsulphone and bisphenol A is evidence that document (1) is a very broad teaching which encompasses many combinations of starting polymers within formula (II)

and sulphonation reagents and that not any of these combinations is actually compatible. That the scope of document (1) is very broad is confirmed by the fact that the sulphonating conditions, namely temperature, duration of reaction and concentration of the reagents, are only broadly defined and have to be adjusted to the solvent, to the polymer and to the sulphonating agent (column 2, lines 31 to 49).

Nothing in the prior art suggests thus a possible correlation between the structure of a specific polymer of formula (II) and the suitability of a particular sulphonation reagent. In absence of such information the skilled man is thus more likely to choose a sulphonating agent in line with the preferred embodiments of the prior art, thus chlorosulphonic acid, and only consider sulphuric acid as a remote alternative. Therefore, the use of this acid together with a specific combination of reactive and non-reactive units must be regarded as inventive.

9. Additionally, the resulting combination of specific recurrent units and selective distribution of sulphonic groups in the claimed polymers surprisingly confers superior properties to the membranes prepared from these polymers.

The first advantage objectively demonstrated by the Respondent with comparative examples filed on 21 March 1988 is a higher burst strength. This parameter was compared for membranes obtained from two sulphonated prior art polysulphones (S-Udel 1700/1 and S-Udel 3500/1) and for membranes from three polymers according to the patent-in-suit with various A:B ratios; if one normalises the results for a thickness of one micrometer, one obtains a burst strength expressed in kPa/ μm of 1.92 and 1.03 for the first group, 3.44, 4.86 and 3.70 for the second group. The latter values would be compatible with the requirements for

reverse osmosis where very thin membranes must be able to withstand hydrostatic pressure without bursting.

Besides, the polymers according to the patent-in-suit exhibit a high glass transition temperature. Whereas T_g determined for a heating rate of $20^\circ\text{C}/\text{min}$ is only 204 and 232 for S-Udel 1700/1 and 3500/1 polysulphones, it is 248 and 291 for the claimed polymers with A:B ratios of 18:82 and 40:60. Although this parameter is not directly relevant for the ion exchange capacity of the membrane, it has a beneficial effect on the behaviour of the polymer at high temperatures as shown by the results of compared dynamic mechanical analysis which are all in favour of the claimed products. In particular, even at the glass transition temperature of the polymer, membranes according to the patent-in-suit retain 80% of their original strength. This thermal stability suggests applications which normally require high temperatures, such as gas separation, as well as current maintenance operations, such as cleaning or sterilization of membranes with steam.

It has not been put forward, nor is the Board aware thereof, that the improvement of these two physical properties, which is the technical problem underlying the patent-in-suit, could actually have been achieved by means of mere structural modifications. The solution claimed by the Appellant involves therefore an inventive step.

10. During oral proceedings the Appellant repeatedly put forward that high burst strength and glass transition temperature do not justify by themselves that an inventive step be acknowledged, since these parameters do not necessarily mean long term stability which should be regarded as the first qualitative criterion for a membrane. In this regard the Appellant objected that this particular advantage had never been demonstrated hitherto.

First of all, the critical importance of long term stability has never been demonstrated by the Appellant who had the onus of proof; but even if such evidence had been provided, the objection to be acceptable would have required comparative data showing the loss of properties for prior art membranes and for membranes obtained from copolymers within the patent-in-suit. In absence of such evidence the Appellant's unsubstantiated assertion cannot be regarded as an argument against the allowability of the product claims.

11. Claims 2 to 5 and 7 are concerned with preferred embodiments of the copolymer according to Claim 1 and of the process according to Claim 6. Their patentability is supported by that of these two claims.

Order

For these reasons, it is decided that:

The appeal is rejected.

The Registrar:



The Chairman:



P.F.