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Bezeichnung der Erfindung: Sulphonated polyaryletherketones
Title of invention:
Titre de l'invention :

Klassifikation / Classification / Classement : C 08G 65/48

ENTSCHEIDUNG / DECISION
vom / of / du 14 April 1988

Anmelder / Applicant / Demandeur : ICI PLC

Patentinhaber / Proprietor of the patent /
Titulaire du brevet :

Einsprechender / Opponent / Opposant :

Stichwort / Headword / Référence :

EPÜ / EPC / CBE Article 56

Kennwort / Keyword / Mot clé : "Inventive step (denied)"

Leitsatz / Headnote / Sommaire

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Case Number : T 90/85 - 3.3.1.

D E C I S I O N
of the Technical Board of Appeal 3.3.1
of 14 April 1988

Appellant : IMPERIAL CHEMICAL INDUSTRIES PLC
Imperial Chemical House
Millbank
London SW1P 3JF
GB

Representative : James, David Gomer
Imperial Chemical Industries PLC
Legal Department: Patents
PO Box 6
Welwyn Garden City
Herts, AL7 1HD
GB

Decision under appeal : **Decision of Examining Division 012 of the European Patent Office dated 12 November 1984 refusing European patent application No. 81 302 145.8 pursuant to Article 97(1) EPC**

Composition of the Board :

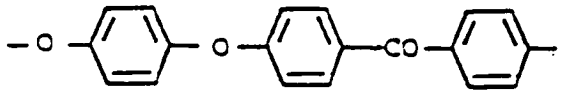
Chairman : K. Jahn
Members : C. Gérardin
P. Ford

Summary of Facts and Submissions

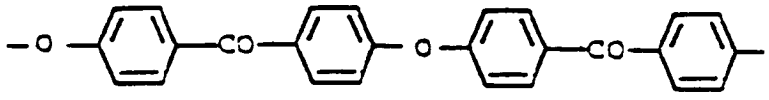
I. European patent application No. 81 302 145.8, filed on 14 May 1981, claiming priority of a prior application on 10 June 1980 (GB 8018915) and published on 16 December 1981 under the publication number No. 41780, was refused by a decision of the Examining Division dated 12 November 1984.

II. The decision was based on nine claims filed on 5 August 1983 of which Claim 1 drafted as product claim and Claim 8 as independent process claim read as follows:

Claim 1: "A polyaryletherketone copolymer which is a hydrophilic sulphonated copolymer derived by controllably sulphonating a copolymer having repeat units of formula

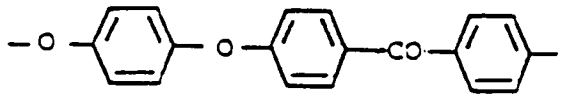
A 

together with repeat units of formula

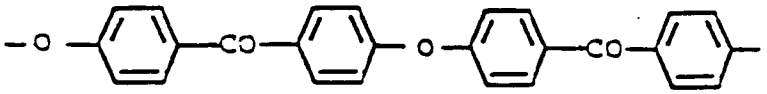
B 

at least 70% of the units A being sulphonated after sulphonation and substantially all the units B remaining non-sulphonated after sulphonation, the control being effected by varying the proportion of the repeat units B in the copolymer of repeat units A and B."

Claim 8: "A process for the production of a hydrophilic sulphonated polyaryletherketone copolymer which comprises controllably sulphonating using concentrated sulphuric acid (98% w/w) at ⩾ 50°C a copolymer having repeat units of formula

A 

together with repeat units of formula

B 

to produce a sulphonated copolymer in which at least 70% of the repeat units A are sulphonated and substantially all the repeat units B are non-sulphonated, the control being effected by varying the proportion of the repeat units B in the copolymer of repeat units A and B."

III. The reason given for the decision to refuse was that the subject-matter of Claims 1 and 8 did not involve an inventive step with regard to the teaching of EP-A1-8895 (document (1)) and EP-A1-1879 (document (2)).

More specifically, it was stated that sulphonation with sulphuric acid of polyaryletherketones described in document (1) occurred only on the hydroquinone units whereas the benzophenone ether units remained unaffected.

Since a copolymer having both recurrent units (A) and (B) according to the application was known from document (2), it was self-evident that the sulphonation thereof would only take place on hydroquinone units; this selective reactivity to sulphuric acid would lead the skilled man to control the degree of sulphonation by the ratio A:B. In order to improve the rather slow sulphonation reaction observed at ambient temperature in the examples of document (1) it was regarded as obvious to raise the temperature.

IV. On 2 January 1985 the Appellant (Applicant) lodged an appeal against the decision by telex which was confirmed by letter on 7 January 1985 and paid the prescribed fee. The arguments presented in the Statement of Grounds filed on 6 March 1985, in the reply to a communication of the Board and in oral proceedings held on 19 April 1988 can be summarised as follows:

(i) From the poor reactivity to sulphonic acid of the homopolymer based on recurrent units A disclosed in Examples 1 and 2 of document (1) the skilled man would conclude that the presence of carbonyl groups resulted in a reduced ability of the hydroquinone residues to be sulphonated. There would thus be a prejudice against a combination of units A and B since the latter would even increase the proportion of deactivating groups.

(ii) In spite of an apparent similarity of the structures derived from diphenylsulphone and benzophenone, theoretical considerations based on the mechanisms of Friedel-Crafts reactions and electrophilic substitution reactions in benzenoid compounds would suggest a difference in their ability to be protonated. Whereas the diphenylsulphone units would

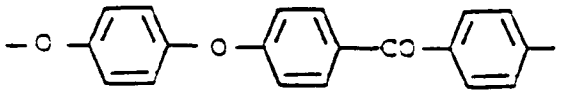
be inert in acid medium, the polarisation of the carbonyl group would favour the protonation of the diphenylketone which would cause the aromatic polyetherketones to depolymerise. Therefore, the skilled man would not confidently expect that polyarylketones would resist degradation to the same extent as polyarylsulphones.

(iii) The closest prior art was in fact US-A-3 709 841 (document (3)) which disclosed the use of chlorosulphonic acid as specific sulphonation reagent to sulphonate a broad class of polyaryl-ethersulphones wherein no difference was made between phenylene, diphenylsulphone and diphenyl-ketone radicals. There was thus no incentive for the skilled man to use sulphuric acid.

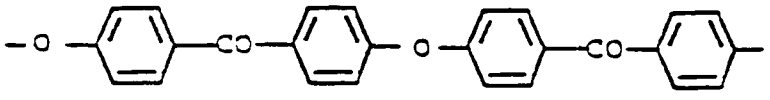
(iv) The presence of ketone units increased the crystallinity of the copolymer and thereby reduced the solubility thereof in organic solvents. Moreover, by sulphonating substantially all the hydroquinone units, one would obviate all the drawbacks bound to the presence of such unsubstituted rings liable to be attacked by chlorine. Tolerance to chlorine was of great importance since the use thereof provided very quick methods of foulant layer removal and facilitated sanitizing membranes. The combination of the above features extended the properties of the known polymers so as to afford a repertoire of membranes from which the optimal one could be chosen according to the specifity of the application.

V. During oral proceedings the Appellant submitted a new Claim 1 which reads as follows:

"A polyaryletherketone copolymer which is a hydrophilic sulphonated copolymer derived by controllably sulphonating, using concentrated sulphuric acid (98% w/w) at $\geq$ 50°C, a copolymer having 5 to 80 mole % repeat units of formula

A 

together with correspondingly 95 to 20 mole % of repeat units of formula

B 

substantially all the units A being sulphonated after sulphonation and substantially all the units B remaining non-sulphonated after sulphonation, the control being effected by varying the proportion of the repeat units B in the copolymer of repeat units A and B."

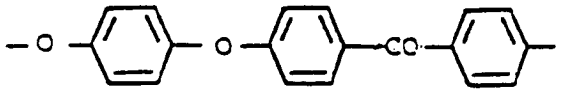
VI. The Appellant requested the impugned decision be set aside and the grant of a patent on the basis of Claim 1 filed during oral proceedings and Claims 4 to 9 as filed on 5 August 1983.

Reasons for the Decision

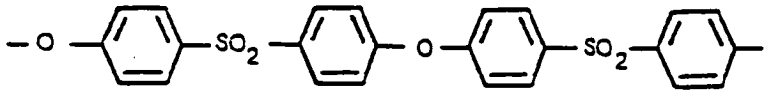
1. The appeal complies with Articles 106 to 108 and Rule 64 EPC and is, therefore, admissible.

2. There are no formal objections on the basis of Article 123 EPC to the current version of the claims since Claim 1 merely combines the features of previous Claims 1 to 3 and further specifies the use of concentrated sulphuric acid at temperature of at least 50°C, which are both process features from Claims 8 and 9 as filed.

3. The disputed patent relates to sulphonated polyaryletherketones intended for use as membrane materials. The closest prior art is represented by document (1) which describes hydrophilic sulphonated copolymers having the repeat unit of formula

A 

in conjunction with the repeat unit of formula

B 

wherein up to 90% of the hydroquinone radicals in repeat unit A carry one sulphonic group (Claims 1 and 2). These hydrophilic copolymers, which are obtained by sulphonation at ambient temperature with sulphuric acid (98% w/w) of the

corresponding non-sulphonated copolymers (cf. Claim 9 and all examples), are suitable for the manufacture of membranes which exhibit satisfactory properties in terms of ion exchange capacity and strength in wet state (page 3, lines 10 to 17). However, because of sulphonation of the hydroquinone sub-units limited to 90%, they are susceptible to attack by chlorine and organic solvents which limits their useful life.

4. In the light of this closest prior art, the technical problem underlying the application can be seen in providing a hydrophilic sulphonated copolymer as well as a process for the preparation thereof with a better resistance to the chemicals mentioned without impairing the ion exchange capacity and the strength of the membrane in the wet state.

This problem is solved according to Claim 1 by substituting the above unit B containing sulphone groups by its counterpart containing ketone groups and by sulphonating all the hydroquinone radicals. As far as the process is concerned, the sulphonation reaction is carried out at temperatures of at least 50°C and the amount of sulphonic groups in the copolymer is adjusted by varying the proportion of the repeat units B therein.

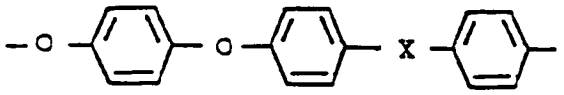
In view of the large field of applications which can be envisaged for the membranes on the basis of their properties as well as of the examples in the description, the Board is satisfied that the above defined technical problem has been plausibly solved.

5. The solutions claimed by the Appellant are not to be found in any prior art document so that novelty is acknowledged.

Since the Examining Division has not raised the issue of novelty, further considerations in this respect are superfluous.

6. It has thus to be examined whether the subject-matter of the present application as defined in the independent Claims 1 and 6 involves an inventive step with regard to the teaching of the cited documents.

6.1 As mentioned above, document (1) relates to the controlled sulphonation of polyarylether copolymers containing both ketone and sulphone linkages. According to this disclosure, (page 1, lines 4 to 30) polyarylethers containing the repeat unit of formula

A 

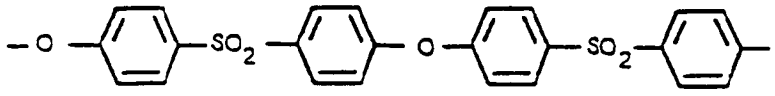
wherein X is a sulphone or a ketone group, undergo the following sulphonation reactions in concentrated sulphuric acid (98% w/w):

(a) when X is SO_2, sulphonation is very fast and yields a completely water-soluble product;

(b) when X is CO, although dissolution of the polymer occurs, sulphonation is much slower;

(c) in both cases sulphonation takes place on the hydroquinone sub-units only.

Additionally, polyarylethersulphones containing only the repeat unit of formula

B 

are virtually non-susceptible to sulphonation under the same conditions. Consequently, polyaryletherketone/sulphone copolymers containing the former repeat unit A in which X is a ketone group and the latter unit B may be controllably sulphonated in concentrated sulphuric acid to give hydrophilic sulphonated copolymers (page 2, lines 1 to 18). This means that controlled sulphonation is achieved by a combination of specific recurrent units with selective reactivity to concentrated sulphuric acid.

6.2 Although document (2) is basically concerned with the preparation of aromatic polyetherketones with hydroquinone radicals, especially the copolymer consisting specifically of the two repeat units according to Claim 1 of the application (see document (2), Claims 1 and 4 as well as Example 14), it mentions as methods of determination of the molecular weight the measurement of the reduced viscosity and inherent viscosity of solutions of the polymer in sulphuric acid.

Reduced viscosity is usually measured at 25°C on a solution of the polymer in concentrated sulphuric, said solution containing 1 gram of polymer per 100 cm of solution (page 1, lines 23 to 28). However, this method is somewhat inconvenient because the measurement needs to be taken immediately after dissolution is complete, the reduced viscosity value obtained using a 1% solution tending to increase with time due to the effect of sulphonation (page 2, lines 5 to 11).

From the drawback of this analytical method of measurement of the molecular weight the skilled man knew that aromatic polyetherketones with hydroquinone radicals could be sulphonated with sulphuric acid without undesirable side reactions or risk of depolymerisation.

6.3 The theoretical considerations based on Electrophilic Substitution in Benzenoid Compounds by R.O.C. NORMAN and R. TAYLOR, Elsevier Publishing Company, 1965, pages 230 to 233 (document (5)) and Friedel-Crafts and Related Reactions by G.A. OLAH, Interscience Publishers, 1964, III, Part 2, Chapter XL, pages 1323 to 1325 (document (6)) put forward by the Appellant in an attempt to demonstrate potential hazards connected with instability of the benzophenone sub-units in presence of concentrated sulphuric acid, do not establish that there was a prejudice against the use of this acid as an agent for the sulphonation of aromatic polyetherketones.

Document (5) concerns kinetic studies of acid-catalysed protodeacylation of acetomesitylene and 2,6-dimethylacetophenone in sulphuric acid to give acetic acid and the corresponding hydrocarbons. The fact that the former compound reacts much faster is attributed to the activating effect of p-methyl group which suggests an electrophilic reaction mechanism (page 232, paragraph 2). This structural requirement is already a fundamental difference with regard to the benzophenone structure and the extension of this teaching to a polymer with benzophenone radicals without the least justification cannot be accepted. The same applies to document (6) since the mere knowledge that the benzoylium ion is more stable than the corresponding benzenesulfonium ion (page 1324, paragraph 3) does not suggest a possible difference of behaviour of sulphuric acid with aromatic polyetherketones and polyethersulphones respectively.

Although the tendency to protonation of ketones due to the polarisation of the carbonyl group is not disputed as such, it does not mean that a polymer containing aromatic ketone sub-units could be expected to actually depolymerise; in any case, the extension to polymers of this cause of instability appears as an oversimplifying approach which disregards the stabilising effect by conjugation of the aromatic polymer backbone.

6.4 In reality, these theoretical considerations cannot outweigh the conclusion from document (1) that in the repeat unit A the reactive sub-unit is the hydroquinone radical, which means that the benzophenone sub-unit is inert to concentrated sulphuric acid at ambient temperature and that consequently the same can be expected from a homopolymer containing the latter sub-unit, thus from a homopolymer of repeat unit B; nor can they outweigh the teaching from document (2), which applies as well to the homopolymers of repeat unit A described in document (1) (page 4, lines 1 to 5), that polyaryletherketones with hydroquinone radicals can be sulphonated with concentrated sulphuric at ambient temperature.

The test results submitted by the Appellant on 6 March 1985 do not provide counter-evidence to these conclusions. The results of experiments at 22°C merely confirm that both the homopolymer of repeat units A and the copolymer lead to suitable products when the sulphonation reaction is performed at ambient temperature. As to the results of the experiments carried out at 80°C, i.e. lower sulphonation ability and higher resistance to degradation for the copolymer, they cannot be regarded as surprising. The additional presence of repeat units B lowers the relative concentration of reactive repeat units A, which means that

the copolymer will be overall less susceptible to sulphonation, and conversely increases the relative amount of benzophenone sub-units known to be inert, which enhances the stability of the copolymer.

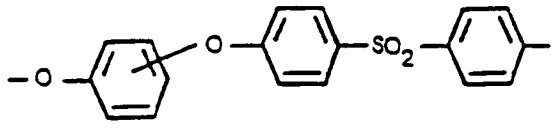
6.5 Nor can document (3), considered by the Appellant as the closest state of the art, lead away from the use of sulphuric acid as sulphonating agent. This disclosure is in fact a very broad teaching both as far as the definition of the polymer to be sulphonated and the sulphonating agents are concerned. It is essential to observe that the starting polymers are basically polyarylethersulphones which can never combine a hydroquinone radical and a carbonyl linkage (column 1, lines 37 to 53) which are the two crucial features in the structure of the polymers presently claimed. More specifically, the radical R can only be present as a carbonyl sub-unit if m is 1 which would correspond to a benzophenone radical; conversely the hydroquinone radical can only be present in the polymer backbone if m is 0, which would actually exclude any carbonyl sub-unit. As to the reactivity of the various aromatic rings, no difference is made between the rings belonging to the diphenylsulphone radical and those belonging to the diphenol radical, which suggests even a statistical distribution of the sulphonic group along the polymer backbone.

Unlike the process claimed in the application, wherein the sulphonation rate depends on the amount of hydroquinone radicals, thus on the ratio A:B, in the copolymer, the amount of sulphonic groups attached in the polyarylethersulphones according to document (3), regardless of the sulphonation process, can be modified by adjusting the sulphonation conditions, i.e. the temperature, the duration of reaction and the concentration of the reagents (column 2, lines 44 to 49). Even if

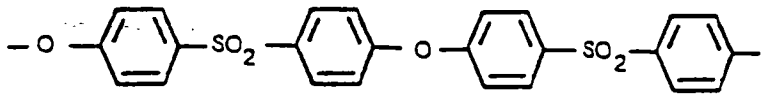
sulphuric acid is not cited as preferred sulphonation reagent, it is mentioned as suitable without any restriction as far as the recurrent units of the polymer are concerned and there is no warning against the possibility of undesired reactions, such as depolymerisation, should the polymer contain carbonyl linkages.

Document (3) teaches thus that temperature is a suitable parameter to control sulphonation; for the skilled man this means that the selection of the most appropriate temperature can be obtained by simple routine experiments for which no inventive step can be acknowledged.

6.6 The alleged stabilising effect against the action of chlorine resulting from the complete sulphonation of the hydroquinone sub-units, put forward by the Appellant for the first time in oral proceedings, has never been substantiated. In particular, it has never been made credible that this effect could be any stronger for the polyaryletherketones presently claimed than for the polyarylethersulphones described in EP-B1-8894 (document (4)). According to this disclosure the controlled sulphonation with concentrated sulphuric acid of a copolymer having the repeat unit of formula

A 

together with the repeat unit of formula

B 

leads to a hydrophilic copolymer wherein substantially all the diphenol radicals are sulphonated (Claim 1). From this teaching the skilled man was thus aware of the potential advantages provided by the complete sulphonation of the otherwise labile hydroquinone sub-units, especially the improved stabilisation to aggressive solvents and to electrophilic reactions in acid medium, all properties which correspond to the problem underlying the application.

6.7 To sum up, neither the choice of sulphuric acid as sulphonating agent nor the adjustment of the temperature up to at least 50°C, nor the complete sulphonation of the hydroquinone sub-units can be regarded as inventive features; in this respect the subject-matter of Claim 6 appears as a mere transposition to the preparation of sulphonated polyaryletherketones of the teachings of documents (1), (3) and (4) wherein the selection of the temperature is a mere problem of optimisation.

As far as the properties of the claimed products are concerned, it is significant that they are described in the application (page 2, line 31 to page 3, line 22) in exactly the same terms as in document (1) (page 3, lines 5 to 26) and in document (4) (page 3, lines 4 to 17). Sulphonated polyaryletherketones, polyaryletherketones/sulphones and polyarylethersulphones which all exhibit a degree of hydrophilicity corresponding to a water absorption capacity at ambient temperature of about 2 weight % water absorption to complete solubility in water, are potentially useful as

membrane materials for ultra-filtration process, desalination and removal of micro-organisms, retain considerable strength even when containing a significant quantity of water, and are suitable for the preparation of ionomers by conversion of the sulphonic acid groups to salts. In this regard, the description of the application does not suggest the least specificity for the present membranes.

The identity of applications explicitly envisaged in the three descriptions reflects in fact the close similarity of the three polymers; they are all based on the same structural and operative concepts which are the presence of two specific recurrent units, one containing hydroquinone sub-units susceptible to sulphonation in concentrated sulphuric acid and the other being inert, the ratio thereof determining the maximum degree of sulphonation, the actual degree of sulphonation being controlled by the sulphonation conditions. The membranes according to the present application should thus be regarded as merely complementing the water treatment membranes described in documents (1) and (4), affording thereby a repertoire of membranes from which the optimal one could be chosen according to the requirements of a particular separation. It is not disputed that the polyaryletherketones according to the application would be the most crystalline of the three polymers and that specific properties usually associated with higher crystallinity, especially improved chemical resistance and thermal stability, can be expected. However, since surprising advantages going beyond these effects have never been demonstrated, the products themselves do not embody an inventive step.

7. These arguments regarding inventive step apply equally to the other composition Claims 2 to 5 as well as to the process Claim 7 which merely represent preferred embodiments of Claims 1 and 6.

Order

For the above reasons, it is decided that:

The appeal is dismissed.

The Registrar: The Chairman:

CG.
P.F.

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