

Internal distribution code:

- (A) [] Publication in OJ
(B) [] To Chairmen and Members
(C) [X] To Chairmen

D E C I S I O N
of 18 December 1995

Case Number: T 0758/91 - 3.3.3

Application Number: 86309536.0

Publication Number: 0225800

IPC: C08G 18/77

Language of the proceedings: EN

Title of invention:
Hydrophilic polyurethane/polyurea sponge

Applicant:
MINNESOTA MINING AND MANUFACTURING COMPANY

Opponent:
-

Headword:
-

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step - affirmed after amendment and provision of comparative data"

Decisions cited:
-

Catchword:
-



Case Number: T 0758/91 - 3.3.3

D E C I S I O N
of the Technical Board of Appeal 3.3.3
of 18 December 1995

Appellant:

MINNESOTA MINING AND MANUFACTURING COMPANY
3M Center
P.O. Box 33427
St Paul
Minnesota 55133-3427 (US)

Representative:

Baillie, Iain Cameron
c/o Ladas & Parry
52-54 High Holborn
London WC1V 6RR (GB)

Decision under appeal:

Decision of the Examining Division of the European Patent Office dated 1 February 1991 and issued in writing on 10 April 1991 refusing European application No. 86 309 536.0 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: C. Gérardin
Members: R. Young
M. K. S. Aúz Castro

Summary of Facts and Submissions

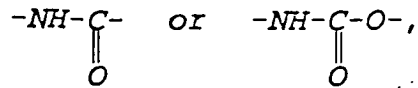
- I. By a decision of the Examining Division, dated 1 February 1991 and issued in writing on 10 April 1991, European patent application No. 86 309 536.0, filed on 8 December 1986 (publication No. 0 225 800), relating to a hydrophilic polyurethane/polyurea sponge, with a Claim 1 reading as follows, was refused.

"A hydrophilic water-absorbing sponge comprising a polyurea or polyurethane and containing at least one sulfonate equivalent per 20,000 molecular weight units, the sulfonate equivalent comprising pendant sulfo groups covalently bonded to the polymer chain, **characterised in that** the sulfonate equivalent comprises a residue of a sulfodicarboxylic acid having said pendant sulfo groups covalently bonded thereto, the carbonyl groups of the sulfodicarboxylic acid residue being linked by ester or amide groups to the polymer chain of said polyurea or polyurethane."

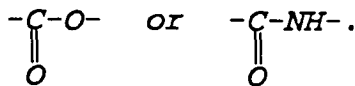
- II. According to the decision, polyurethane foams which were able to absorb water were disclosed in the closest state of the art

DI: EP-A-0 000 724.

These were prepared from polyols containing pendant sulphonated groups. The only difference between the materials of DI and those of the application in suit was the linkage of the sulphonated units to the polymer: whereas according to DI these units were linked via groups



the respective links in the foams according to the application in suit had the structural formula



There was, however, no evidence on file that this minor structural difference gave rise to any technical effect. Consequently, the objective technical problem underlying the application in suit had to be seen as the provision of further polyurethane (urea) foams rendered hydrophilic by means of sulphonate groups. An obvious solution would have been to use any other known hydrophilic starting compound for polyurethane resins which contained a sulphonate group, such as the sulphodicarboxylic acids, polyols or polyamines disclosed in

DIV: EP-A-0 146 326.

The argument that there would have been no incentive to combine DI with DIV was not convincing, since the statement of problem did not require an improvement. Consequently, the claimed subject-matter did not involve an inventive step.

III. On 3 June 1991, the Appellant filed a Notice of Appeal against the above decision, the appeal fee being paid on the same day. The Statement of Grounds of Appeal, filed on 20 August 1991, was accompanied by amended sets of claims forming a main and auxiliary request,

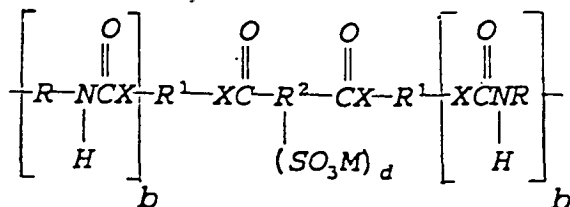
respectively, and also an experimental report in the form of a Declaration by one of the inventors, Wayne K. Larson. Samples of sponges prepared according to the experiments described in the declaration were received on 29 November 1994.

In the Statement of Grounds, the Appellant argued, on the basis of the experimental results in the Declaration, that sponges derived from a sulphonated polyisocyanate in accordance with the teaching of DI had in all cases greatly inferior water absorption properties in comparison with those of the sponges claimed in the application in suit, and that consequently an inventive step should be recognised.

IV. A new set of Claims 1 to 14 was filed on 7 June 1995 in replacement of the two sets of claims previously on file, followed by an amended version of Claims 1 and 11 on 4 December 1995, in response to communications issued by the Board on 16 February and 7 November 1995 respectively.

Independent Claims 1, 11 and 14 of the final version read, respectively, as follows:

"1. A hydrophilic water-absorbing sponge comprising a polymer of urea and/or urethane and incorporating at least one sulfonate equivalent per 20,000 molecular weight units, characterized in that the polymer comprises a plurality of units having the formula



wherein

R is an organic group having a valence of 2, 3 or 4 selected from linear and branched aliphatic groups having 2 to 12 carbon atoms, and 5- and 6-membered aliphatic and aromatic carbocyclic groups having 5 to 50 carbon atoms;

each R¹ is independently a linear or branched organic group having a valence of (b + 1) consisting of a chain of up to 110 carbon atoms in units selected from linear groups C_nH_{2n} and C_nH_{2n-2} in which n is 2 to 12, 5- or 6-membered carbocyclic groups, and aromatic groups of 5 to 20 carbon atoms, which are

separated by ether oxygen atoms, or $\begin{array}{c} \text{O} \\ \parallel \\ -\text{OC}- \end{array}$, or $\begin{array}{c} \text{O} \\ \parallel \\ -\text{NHC}- \end{array}$ groups, the linear or branched organic group having a molecular weight of up to 2 000, wherein b is an integer of 1, 2 or 3; and

R² has a valence of d + 2 and is an arenepolyyl group (polyvalent arene group) having 6 to 20 carbon atoms or an alkanepolyyl (polyvalent alkane) group having 2 to 20 carbon atoms,

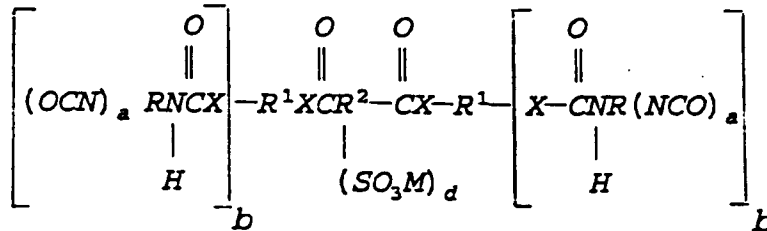
wherein d is a number 1, 2 or 3,

X is independently -O- or -NH-, and

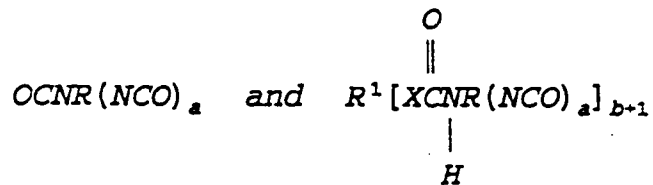
M is a cation.

11. A method of preparing a sponge comprising the steps of

- (a) providing an isocyanate-terminated sulfopolyurethane/urea comprising a compound having the formula



and, optionally, at least one of compounds having the formulae



wherein a is an integer of 1 to 3, b is an integer of 1 to 3, and R, R¹, R², X and M are as defined in Claim 1;

- (b) reacting said sulfopolyurethane/urea with at least one of
- (a) water, and
 - (b) at least one of a polyol or polyamine plus a blowing agent, and
 - (c) isolating the resulting sponge.

said sponge incorporating at least one sulfonate equivalent per 20,000 molecular weight.

14. Use of a sponge as claimed in any of claims 1 to 10 to absorb an aqueous liquid."

Claims 2 to 10 are dependent claims relating to elaborations of the sponge according to Claim 1 and Claims 12 and 13 are dependent claims relating to elaborations of the method of Claim 11.

V. The Appellant requests that the decision under appeal be set aside and a patent granted on the basis of the following claims:

Claims 1 and 2 (part) and Claims 8 to 11 (part) filed on 4 December 1995 (letter of 30 November 1995);

Claims 2 (part) to 7 and Claims 11 (part) to 14, filed on 7 June 1995 (letter of 6 June 1995); or, in the alternative, oral proceedings.

A previous request for the refund of the appeal fee (Statement of Grounds of Appeal, page 4) was withdrawn (submission of 7 June 1995, page 3).

Reasons for the Decision

1. The appeal is admissible.
2. Allowability of the amendments

Claim 1 is supported by Claims 1 and 2 of the application as

filed, the reference to "ether atoms, or $\overset{\text{O}}{\parallel}\text{-OC-}$, or $\text{-NHC-}\overset{\text{O}}{\parallel}$ groups" in the definition of R¹ being based on the description as originally filed on page 4 at line 29 ("polyether, polyester or polyamide polyol"). Claim 2 is based on Claim 3 as originally filed. Claims 3 to 10 are based on Claims 7 to 14 respectively as originally filed. Claim 11 is based on original Claim 15 and incorporates the feature of at least one sulphonate equivalent per 20,000 molecular weight units specified on page 2, lines 10 to 14 of the application as originally filed. Claim 12 is based on the flow chart of page 8 of the application as filed. Claim 13 is based on original Claim 16 and Claim 14 is a use claim based on original Claim 17, with the term "aqueous liquid" being based on "liquid" in original Claim 17, read in the light of the references to "water-absorbing sponge" in original Claim 1 and the general reference to "hydrophilic polyurethane/polyurea sponge" in the opening paragraph as filed.

Consequently, the independent claims have been restricted to specify precisely the nature of the repeating unit which is to be present in the urethane or urea polymer. No objections arise in respect of Article 123(2) EPC.

3. *The closest state of the art; the technical problem*

The application in suit concerns a hydrophilic urethane/urea polymer sponge containing at least one sulfonate equivalent per 20,000 molecular weight units of the polymer. Such foam materials are, however, known from DI, which is considered to be the closest state of the art.

- 3.1 According to DI, compounds having at least one hydroxy group and at least one urethano-aryl-sulphonic acid group have an average molecular weight of 300 to 12,000 (Claim 1).

The compounds preferably contain a structural unit of the general formula:



in which

R_1 is a divalent to hexavalent radical of a polyol, e.g. a polyester, polyether, polythioether or polyesteramide and

Ar is a polyvalent radical of an aromatic isocyanate (page 3, lines 12 to 25).

The compounds may be prepared by reacting compounds having at least two OH groups and of molecular weight 62 to 10,000 at 0-190°C with aromatic isocyanatosulphonic acids, whereby the ratio of total NCO groups (including any which may be in dimerized form) to sulphonic groups is 0.5 to 50 and the equivalent ratio of the sum of the OH-groups of the OH group-containing compound to NCO-groups is 1.5 to 30 (Claim 4).

The compounds may be used as coreactants with polyisocyanates in the preparation of polyurethane foams, so that surfactants, such as polysiloxanes, which provide reactant compatibility and foam stabilization, can be done away with. There is thus provided a polyol of higher polarity and hydrophilic character, resulting in a polyurethane of improved fire resistance and which is biologically degradable (page 1, line 11 to page 2, line 30).

The OH-containing starting material can be a low molecular weight glycol, polyester, polyether, polyester-amide, or a polyether which has been grafted with vinyl monomers, etc. (page 5, lines 16 to 28).

The preferred isocyanatosulphonic acids are the sulphonation products of 2, 4-toluene diisocyanate, or the mixed 2, 4- and 2, 5- isomers, or of the di- or polyisocyanates obtained by phosgenation of aniline-formaldehyde condensates, or diisocyanatodiphenylmethane (page 11, lines 12 to 31).

The sulphonate groups can be neutralised with a base (page 16, line 24 to page 17, line 12).

Examples 14 to 17 relate to the preparation of polyurethane foams by a reaction involving a sulpho-polyol B, C, D or E with a modified toluene diisocyanate, water and alkanolamines in the presence of a catalyst. The sulpho-polyols are themselves prepared by reaction of a diisocyanatoluenesulphonic acid with various polyoxyalkyleneglycolethers (Examples 5, 10), the product then being neutralized with methanolic KOH (Examples 8, 11), triethylamine (Example 12) or N,N-dihydroxyethylolylethylamine (Example 13). The mixing time, foam rise time and time to non-tackiness of the

resulting polyurethane foams are quicker than in a comparative experiment in which a non-sulpho polyol A is used.

- 3.2 Compared with this state of the art, the technical problem underlying the application in suit is seen in the provision of a hydrophilic sponge of improved water absorption properties, both in terms of absolute amount of water absorbed and efficiency of water absorption (wipability).
- 3.3 The solution proposed according to Claim 1 of the application in suit is to replace the polymer from which the foam of DI is made, by one comprising a plurality of units having the formula defined in Claim 1 of the application in suit. This is achievable in practice by replacing the isocyanate-reactive hydroxy-terminated urethano-aryl-sulphonic acid starting material of DI, by an isocyanate-terminated sulphopolyurethane/polyurea of the formula defined in Claim 11 and reacting the latter with water, a polyol or polyamine and a blowing agent to form a polyurethane/polyurea sponge.
- 3.4 It can be seen from the comparative test report belonging to the Declaration by Larson, filed with the Statement of Grounds of Appeal, that a sponge prepared according to the most relevant Examples 14 and 15 of US-A-4 174 434 (corresponding to DI) had extremely inferior water absorption and wiping properties (Examples D and E, Table I on page 9 of the Declaration), compared with a sponge prepared according to Example 3 of the application in suit (Table II). This improvement is even more marked over variants of DI which nevertheless lie closer to the example of the application in suit, in that the polyether chain component is made from ethylene oxide rather than propylene oxide (Table II, Examples F and G). The

description of the foams produced is moreover corroborated by the samples filed on 29 November 1994.

Consequently, it is credible to the Board that the claimed measures are effective to solve the technical problem.

4. *Novelty*

The decision under appeal recognised novelty in the claimed subject matter. This subject-matter has been further restricted (Section 2, above).

The Board also considers the subject-matter claimed in the application to be novel.

5. *Inventive step*

It is necessary to examine whether the skilled person, starting from DI, would have expected improved water absorption and wiping properties to result from replacing the hydroxy-terminated urethano-aryl-sulphonic acid starting material of DI by the isocyanate terminated sulphopolyurethane/polyurea according to of the formula defined in Claim 11 and reacting the latter with water, a polyol or polyamine and a blowing agent to form a polyurethane/polyurea sponge comprising structural units as defined in the solution of the technical problem (Section 3.3, above).

- 5.1 There is no suggestion in DI to make such a modification for any purpose, let alone to improve the water absorption properties.

Consequently, there is no hint in the disclosure of DI to the solution of the technical problem.

5.2 Of the other documents cited, the only one which discloses a sulphodicarboxylic acid of the kind forming the basis of the structural units according to Claim 1 is DIV.

According to DIV, a low molecular weight (i.e., less than 6,500) film-forming, polymerizable, ethylenically unsaturated sulphocompound that is hydrophilic and solvent soluble (soluble in both water and organic solvents) but is readily converted on exposure to actinic radiation to a polymer that is solvent insoluble (not soluble in water, organic solvents, or mixtures thereof), and in certain examples, is hydrophobic, is the poly(ethylenically unsaturated ester or amide) of a sulphopolyol or sulphopolyamine. This comprises the reaction product of one mole of a sulphodicarboxylic acid and two moles of an aliphatic polyether- or polyester-polyol or polyamine having a molecular weight <1,000 and two to four OH- or amine groups, the sulphocompound having an ethylenic unsaturated functionality of 2 to 18 and an equivalent weight per ethylenic unsaturated functionality of <2,500 (pages 2, lines 8 to 25 and Claim 1).

The product of this reaction is not stated to be foamable, let alone capable of forming a sponge (an open-celled foam) as claimed in the application in suit. On the contrary, although the requirement for the presence of ethylenic unsaturation may be fulfilled by further reaction with an isocyanate, it is a requirement that after the reaction no isocyanate groups remain (page 2, line 26 to page 6, line 4, especially page 6, lines 1 to 4).

Consequently, the formation of an isocyanate-terminated prepolymer of the kind necessary for the solution of the

technical problem is, according to the relevant disclosure of DIV, excluded.

Consequently, there is no hint to the solution of the stated problem in DIV either.

5.3 In summary, the solution of the technical problem does not arise in an obvious way from the state of the art.

Hence, the subject-matter of Claim 1 and, by the same token, of the dependent Claims 2 to 10 is not only novel, but involves an inventive step.

5.4 The method according to Claim 11 will necessarily result in a sponge comprising the structural units defined according to Claim 1.

Consequently, for the same reasons as given in relation to Claim 1, above, the subject-matter of Claim 11, and by the same token that of dependent Claims 12 and 13 is novel and involves an inventive step.

5.5 Similarly, the use, according to Claim 14, of a sponge as defined in Claim 1, which involves superior water absorption and wiping properties, must also be inventive. Thus the subject-matter of Claim 14 is novel and involves an inventive step.

6. It will, however, be necessary for the description to be adapted to the revised claims. Consequently the Board intends to refer the case back to the first instance.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.
2. The application is referred back to the first instance with the order to grant a patent on the basis of Claims 1 to 14 as specified in Section V, above, and a description yet to be adapted.

The Registrar:



E. Gorgmaier

The Chairman:



C. Gérardin